

Integrated Master in Bioengineering

Branch of Biological Engineering



Long-term wine bottling comparison

Master's Thesis

of

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conducted in

I&D Department

Cork Supply



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Resumo

O tipo de rolha utilizado durante o engarrafamento é da maior importância para a evolução qualitativa do vinho. A cortiça é a escolha natural, mas ao longo dos anos outras alternativas têm sido testadas. Nesta Tese, dois tipos de vinho foram engarrafados utilizando seis rolhas diferentes: uma rolha NATURAL e cinco rolhas técnicas: VINC, VINC +, D3, D5 e DNT. O VINC e o VINC + são rolhas técnicas micro-aglomeradas lançadas pelo grupo Cork Supply, fabricadas a partir de granulados de cortiça. Os efeitos de longo prazo do uso de diferentes rolhas foram avaliados durante um ano de engarrafamento. O desempenho destas foi avaliado quanto aos aspectos físicos realizadas sobre as rolhas (força de extração, recuperação do diâmetro após extração, absorção), à composição do vinho (SO_2 livre e total; acidez volátil) e às propriedades sensoriais utilizando, principalmente, a ferramenta Napping® com Ultra-Flash Profiling. No que diz respeito às medições físicas, a força de extração e recuperação não indicaram uma tendência de evolução ao longo do tempo. O parâmetro absorção mostra as principais diferenças (houve um aumento ao longo do tempo para cada rolha), mais perceptível nas rolhas naturais do que nas outras. As correlações de Pearson revelaram uma correlação negativa entre a recuperação do diâmetro após extração e a absorção. Nem o SO_2 livre e total, durante o tempo de engarrafamento, nem a acidez volátil predizem uma degradação do vinho. No entanto, o vinho tinto começou a ter um decréscimo incremental de SO_2 livre, oito meses após o engarrafamento. A análise sensorial também mostra diferenças entre vinhos com a rolha NATURAL e as outras, com o Napping® a exibir também algumas variações entre as rolhas técnicas. No vinho branco, o que possuía a rolha D5 foi aparentemente mais intenso em atributos do tipo fruta e no vinho tinto, o que possuía a rolha NATURAL esteve relacionado com um aroma “cereja” aos 8 e 12 meses. Todos eles mostraram uma preservação dos caracteres varietais (característico do vinho) e mantiveram o SO_2 estável. No final de um período de engarrafamento de um ano, foi realizado um dendrograma e este projetou, com todos os dados utilizados, um comportamento baseado na percentagem de cortiça, ou seja, a posição de todos a rolha era hierárquica juntando D3 e D5, VINC e VINC +, DNT, longínquas da rolha NATURAL. Este é um estudo em andamento, já que um ano de engarrafamento é curto para conclusões definitivas. Até agora, não existem diferenças significativas entre as rolhas técnicas, apenas entre a NATURAL e as outras cinco.

Abstract

The type of closure used during bottling is of the utmost importance for the quality and endurance of the wine. Cork is the natural choice, but over the years manufactured alternatives are being tested. In this Thesis, two types of wine were bottled using six different closures: one NATURAL cork stopper and five technical stoppers: VINC, VINC+, D3, D5 and DNT. VINC and VINC+ are micro-agglomerated technical stoppers launched by Cork Supply Group, manufactured from cork granulates. Long-term effects of the using of different closures were evaluated during one year of bottling. Closure performance was assessed for physical aspects (extraction, rebound recovery, absorption), for wine composition (chemical - free and total SO₂; volatile acidity) and sensory properties using, mainly, the Napping® tool with Ultra-Flash Profiling. Regarding physical measurements, the extraction force and rebound recovery of the stoppers did not indicate a tendency over time. Absorption shows the major differences (there was an increase over time for each closure), more noticeable between the NATURAL and the others. Pearson correlations revealed a negative correlation between rebound recovery and absorption. Neither the free and total SO₂ during the time of bottling nor the volatile acidity predict a degradation of wine. However, red wine began to have an incremental decrease of free SO₂, eight months after bottling. Sensorial analysis also shows differences between wine with NATURAL closure and others, with Napping® also exhibiting some variances among the technical ones. In white wine, D5 closure was apparently more intense in fruit-type attributes and in red wine NATURAL issued a “cherry” aroma at 8 and 12 months. They showed a preservation of the varietal characters (characteristic of each wine) and kept the deleterious sulfides at residual levels. At the final of a one-year bottling period, a cluster dendrogram was performed and projected a “cork-like” behavior with all data used, i.e., the position of all closures was hierarchical joining D3 and D5, VINC and VINC+, DNT, all further apart from the NATURAL stopper. It is an ongoing study since a year of bottling is short-time for definite conclusions. Until now, there are no significant differences between the technical stoppers, only between NATURAL and the other five.

Declaração

Eu, Maria do Rosário Peixoto Silva Rocha, declaro, sob compromisso de honra, que este trabalho é original e que todas as contribuições não originais foram devidamente referenciadas com identificação da fonte.

Porto, 22 de junho de 2018

(Maria do Rosário Rocha)

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Notation and Glossary

A_{420}	Absorbance at wavelength λ
CSG	Cork Supply Group
CSP	Cork Supply Portugal
CSP1	Cork Supply Portugal 1 - São Paio de Oleiros
CSP2	Cork Supply Portugal 2 - Rio Meão
CSP3	Cork Supply Portugal 3 - Montijo
CSP4	Cork Supply Portugal 4 - São João de Ver
CT	Computed Tomography
CVRVV	Comissão de Viticultura da Região dos Vinhos Verdes
FTIR spectroscopy	Fourier Transform infrared spectroscopy
KW	Kruskal-Wallis
MFA	Multiple Factor Analysis
N.A.	Not applicable
OIV	International Organization of Vine and Wine
PCA	Principal component analysis
SD	Standard deviation
TCA	2,4,6-trichloroanisole
UFP	Ultra-Flash Profiling
VA	Volatile acidity

θ_n	Neck diameter of the bottle
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1 Introduction

1.1 Background and Presentation of the Project

This work is a Master's Thesis project included in the Dissertation of the Master of Bioengineering, Branch of Biological Engineering, which was developed in business environment in the R&D Department of Cork Supply Portugal (CSP), in São Paio de Oleiros and in São João de Ver.

The main goals were the understanding of the long-term effects (physical, chemical and sensory tests) of using different closures (natural corks and technical stoppers) on wine bottling and a final positioning regarding the performance of the closures at twelve months (one year of bottling) based on all assessments. Two types of wines (red and white) were studied under six different stoppers: VINC, VINC+, D3, D5, DNT (all technical stoppers) and NATURAL.

Currently, higher market prices for natural corks and in an attempt to use cork by products, created the demand for alternative corks (Silva et al., 2003). In consonance with that perspective CSP Group releases VINC technical corks (Business Journal 2017) in 2016. These are micro-agglomerated technical (corks manufactured entirely from cork granulates derived from sub-products resulting from the production of natural stoppers) (APCOR 2017b). VINC was the first new product line to be launched from the company's dedicated technical cork facility, Cork Supply Portugal 4 (CSP4), in São João de Ver. In the latter project, VINC used granules sized 0.5-2.0 mm and VINC+ granules sized 0.5-1.0 mm.

However, there is limited information regarding real performance of the alternative stoppers, specifically concerning wine ageing. A one-year comparison study with different physical, mechanical, chemical and sensory tests was proposed to understand the positioning of VINC corks against other technical stoppers on the market, and in opposition to the natural cork (the standard and most used option) that belongs to the CSP group. At sensory level a new technique was applied combining Napping® (a technique that results a product configuration map to show overall how the products were ranked in relation to one another) with Ultra-Flash Profiling (UFP) in order to gain descriptive information on the products, proposed by Perrin et al. (2008).

1.2 Company presentation

The Cork Supply Group (CSG) was founded in 1981 by Jochen Michalski in Northern California's renowned wine region. He returned to the USA, after working in Portuguese Cork Industry, with a new business idea: supply cork stoppers to the best wine producers in the world. The raw material came from Portugal and the finishing processes were done in the USA. This product was an innovation regarding the attention of the details and a careful customer service. Under Mr. Michalski leadership, company expanded with specialized staff and operations. With standard-

setting quality products and service, Cork Supply is nowadays one of the wine industry's largest providers of natural corks, and is the leading natural cork supplier in North America (APCOR 2017a).

CSG has a big proliferation around the world as Cork Supply Portugal, Cork Supply USA, Cork Supply Spain, Cork Supply France, Cork Supply Italy, Cork Supply Argentina, Cork Supply Australia, Cork Supply South Africa, Cork Supply Canada and Cork Supply China (CorkSupply 2017a). Corks are distributed in all wine regions of the world.

In 1995, the CSP was founded. In Portugal the Group has four manufacturing units. Cork Supply Portugal 1 (CSP1) is in São Paio de Oleiros, with newly built facilities in 2007, being the head office of CSP. It is responsible for the stages of manufacturing and production of cork stoppers (washing, coating, manual and electronic choice, packaging and shipping). Besides that, CSP1 has a laboratory with the capacity to execute a wide range of sensorial analysis and equipped for Solid-phase microextraction - Gas chromatography-mass spectrometry (SPME-GC/MS) analysis, where a team of specialized technicians carries out innovative research and development in the cork sector. Cork Supply Portugal 2 (CSP2) is in Rio Meão and is dedicated to printing/branding, surface treatment, packaging and quality control of all cork stoppers sent to wineries throughout Europe. Cork Supply Portugal 3 (CSP3) is located in Montijo and guarantees the cork preparation activities, such as choosing and stabilizing, cooking and shipping to CSP1. CSP4 is in São João de Ver and is responsible for producing technical corks. It is the most recent manufacturing unit (Observador 2016).

In the beginning of the CSP activity, the company's strategy was producing and commercializing for the companies within the Group. Nevertheless, since last decade CSP developed and nowadays the commercial network spreads all over Europe. Besides wines, the company also offers solutions for spirits and other market niches, such as gin or Port wine. The key of development and success of company is the focus on research and development. As leader of quality, Cork Supply redefined a new standard with invention of Innocork®, a process that extracts 2,4,6-trichloroanisole (TCA) and other off-flavors from natural cork (APCOR 2017a).

1.3 Contributions of the Work

Since VINC technical corks are a recent product (2 years old) it was important to assess their real performance in contact with wine, which is considered a crucial step in product development. A perspective of comparing stoppers on the market was never made before in the company nor has using Napping® technique for sensory tests. Therefore, this data can support the positioning of the stoppers facing wine aging, which allows the companies to decide their global processes, for instance if they wish to distance themselves or to approach others.

This project was already in progress when the work for this Thesis began. The bottling of the wine with the different closures was done in March 2017, in a partnership with Quinta do Casal Branco, in Almeirim. I became involved in the project since August 2017. First, it was a part of my work in the curricular unit “Seminários e Projeto de Investigação” and then continuing to my Master Thesis. All physical and sensory tests were done in the company, while the chemical analyzes were carried out at the Comissão de Viticultura da Região dos Vinhos Verdes (CVRVV).

1.4 Organization of the Thesis

This thesis is organized in 6 main sections. To begin with, in section 1, there is an overview of the goals embraced, highlighting their background motivation and importance.

Next, in section 2, a comprehensive description of the state of the art is made regarding cork, specifying cork stoppers and alternatives of it, such as technical corks, as well as fundamentals of wine ageing, chemical properties of wine and sensorial analysis.

Then, in section 3 (“Materials and Methods”) are clarified the procedures and methods used in the project.

Section 4 (“Results and Discussion”) contains the obtained results, as well as their analysis: It is divided into the results of the physical, chemical and sensorial variables, encompassing, in the end, a general perspective and positioning of the products at the end of one year of bottling.

To follow, Section 5 briefly designates the project’s main conclusions, complemented with Section 6 (“Evaluation of the work”), that contains the limitations and some perspectives of future work.

Finally, all the bibliographic references used in this project are presented and the Annexes contain some complementary information of the Thesis studies.

2 State of the Art

2.1 Cork

Cork is a cellular material with closed cells. It was one of the first materials to be observed and described by Robert Hooke (1635-1703). In 1660, for the first time in history, he drew the scheme of cork's cellular organization with hollow structures, that he named "cells". The name of "cells" was born and took a huge place in history, being used until nowadays (Lagorce-Tachon et al., 2015). Cork seems a honeycomb of small closed cells with thin cell walls, organized in a regularly well-ordered and compacted structure (Oliveira et al., 2015a).

Cork is extracted from the cork oak tree (*Quercus suber* L.). A cross-section of a tree stem (Figure 1) shows two main parts: xylem (inner part), located to the inside of the cambium and bark (outer part). The bark has two types of tissues: phloem (food-conducting tissue in the vascular plants) and periderm (three-part layered structure - phellogen; phellem; phelloderm) (Santos et al., 2017).

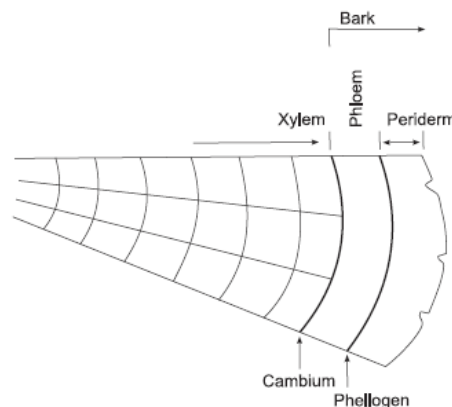


Figure 1 - Cross-section of an oak tree stem (Source: Pereira 2007)

Anatomically, cork is a tissue named phellem and it belongs to periderm, located in the bark system. It is formed by the phellogen to the outside. The main goal of cork is the protection of the living and physiologically active tissues from the outside environment (Santos et al., 2017).

Cork is removed periodically in a sustainable manner, considering the tree's lifetime. During the man-made extraction of cork, the death of the phellogen occurs. However, there is a rapid formation of a traumatic phellogen that resumes its purposes of protective cork layer producer. Cork growth is enhanced in the initial years (after formation) but decreases as the age of the phellogen increases and remains approximately constant for older phellogens. The presence of lenticular channels crossing the cork layers (from the outside to the inside) is the main cause of the heterogeneity on the cork surface. Other factors are the woody inclusions, small fractures and

other defects. All together give information about the porosity of cork and influence the performance of cork products, such as wine stoppers. Some defects are biological or have external origin. Imperfections like wet cork spots, insect galleries or microbial stains are causes to dismiss a natural cork stopper, in which porosity is the basis for the distinctive classification among the natural stoppers (Oliveira et al., 2015a; Oliveira et al., 2015b).

Cork is a biological material with unique properties. Those properties are derived from its chemical composition. The major component is suberin ($\approx 50\%$), a polyester (similar to cutin) composed of long fatty acid chains, hydroxyl fatty acids and phenolic acids linked by ester groups. Lignin ($\approx 30\%$) is the second most important structural component. It also determines the behaviour of cork as a material and the resistance to compression, because it is a hard polymer with covalent bonds. The structural components of the cell walls are cellulose and hemicellulose representing only 10% (Lagorce-Tachon et al., 2015; Pereira 2007; Santos et al., 2017). Chemically there are some extractives including non-polar compounds and polar, mostly phenolic. These extractives represent 10% and because they are easily extractable normally some of them are related with the organoleptic properties of wine (Lagorce-Tachon et al., 2015).

2.2 Cork stoppers

For many years cork has been the most widespread material for wine stoppers and it is considered the standard for quality wines (Juanola et al., 2004). Cork stoppers can combine a good physical performance and durability, as well as allow a balanced development of wine inside the bottle. The advantages of this material are the chemical inertia, high performance insulation taking account a set of physical and mechanical properties and a matchless closure (Oliveira et al., 2015b). Nowadays, there are several types of cork stoppers, such as: natural stoppers, natural multipiece stoppers, colmated natural stoppers, technical stoppers, champagne stoppers, agglomerated stoppers, microgranulated stoppers and capsule stoppers.

Technical closures contain a dense agglomerated cork body and optionally discs of natural cork glued to its top or both ends. This type of stopper is chemically very stable and mechanically highly resistant. In addition, they have demonstrated to be excellent stoppers over time, managing to preserve the required concentration of free SO_2 in the bottle, avoiding early oxidation of the wine while not developing unpleasant reduction aromas. Agglomerated stoppers are manufactured entirely from cork granulates derived from sub-products resulting from the production of natural stoppers. Adding to the economic advantage of lesser-priced wines and high turnover on the market, these stoppers also have the advantage of being totally homogenous within a lot (APCOR 2017a). A sub-division of agglomerated stoppers is the microagglomerated stoppers: these use smaller size cork granules, typically below 3mm in size.

Although the choice of closure is, theoretically, a technical decision based on its sealing properties, wine producers are also influenced by the players in the marketplace and consumers preferences.

2.3 Cork taint in wine

“Cork taint” is a very well-known problem and is described by characteristic musty/moldy odors, which masked all aromas presented regardless its intensity (Tarasov et al., 2017). 2,4,6-trichloroanisole (TCA) is a chemical compound known as the main cause of classical “cork taint” in wines. TCA belongs to the family of haloanisoles. Cork stoppers nowadays are the most known source of wine contamination by haloanisoles (Culleré et al., 2009). Certain fungi can transform some precursors as chlorophenolic biocides to TCA and different chloroanisoles. These compounds can be released to the air and further transmitted to the wine (Jung et al., 2010). TCA has an intense smell, a high volatility and a low perception threshold in wines starting from 1.5-2 ng/L. Wine can be entirely spoiled by presence of that compound above these concentrations. They are sufficient to destroy the aroma composition and make wine undrinkable (Olivella et al., 2012).

2.4 VINC stoppers from Cork Supply

A schematic of the production process of the VINC line is described in Figure 2, whereby the process is started with raw material from and controlled by CSP. The raw material is the “remains” of CSP1 natural corks production. VINC was launched from the company’s dedicated technical cork facility, CSP4. The VINC line is composed of micro-agglomerate technical corks – made with tiny, packed-together cork pieces (Business Journal 2017). The remains of natural cork are transformed into granules and, afterwards, divided by density and by dimensions. The disinfection process follows and is a result of Cork Supply’s improved Vapex® batch-cleaning process. Vapex® is a proven distillation process that effectively extracts TCA from cork granules, before the granules are made into technical corks. Using pressurized steam, Vapex® volatilizes TCA molecules potentially in cork granules, ensuring that only the cleanest quality neutral corkwood is used to produce the company’s technical corks. Thus, they reduce TCA with values less than 0.5 ng/L, or below human-detectable levels. With that, the amount of the common “wine taint” mold compound that can get into wine is scarce (CorkSupply 2017).

The resulting granules are mixed with a glue (the binder) and microspheres. The final process of rectification has the purpose of correcting the size of the stoppers according to the target objective.

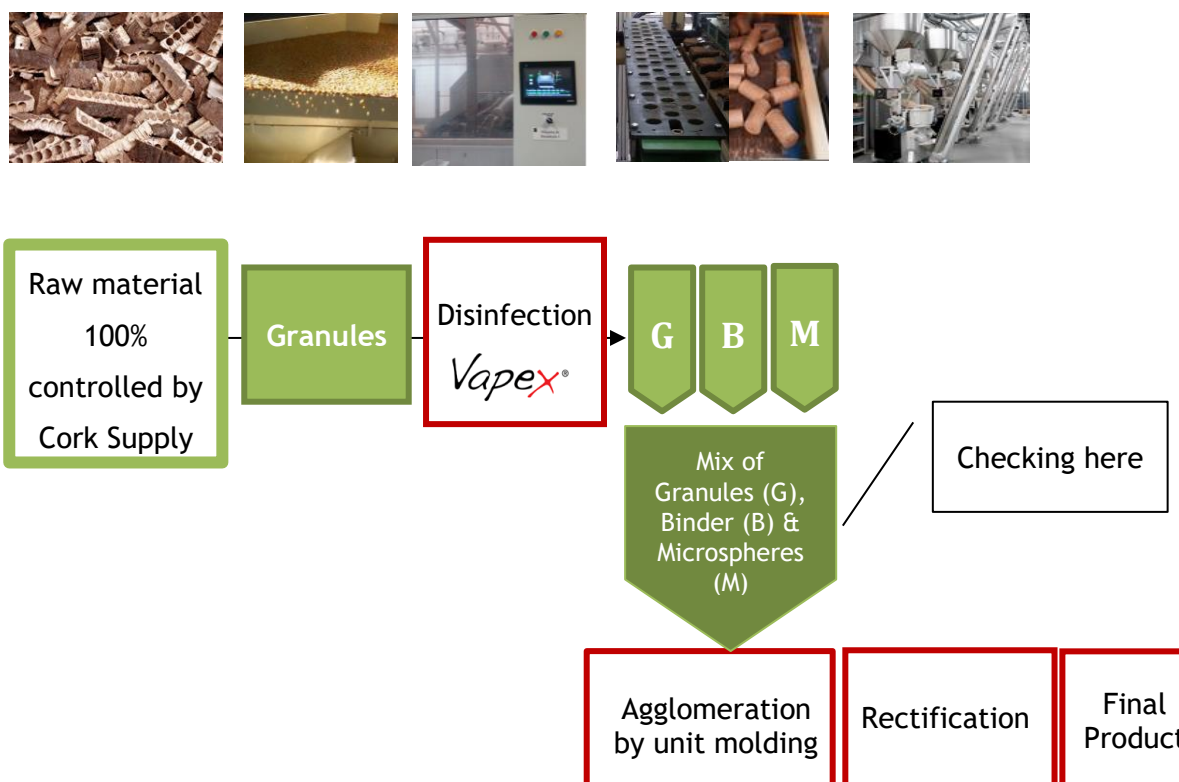


Figure 2 - Scheme of VINC production in CSP4

2.5 Physical and mechanical properties of stoppers

The closures - natural and technical corks - are manufactured with distinct technologies and formulations. Consequently, different behavior is expected at a mechanical and physical level, and this performance is important in view of the consumer's perception (for example, the strength needed to uncork, called extraction force).

The **extraction force** depends on the compressive stress and increases with a larger diameter, comparatively to the internal bottle bore. The absorption is related with the impregnation of the closure with wine and also influences the extraction force of stoppers, reducing the effort to uncork bottles. Regarding natural corks it is important to emphasize that cork is an anisotropic material (directionally dependent, which implies different properties in different directions) due to its specific cell structure and cell orientation. Moreover, the presence of lenticels, running radially, can also reinforce the rigidity of the material when cork is compressed along their growth direction (Lagorce-Tachon et al., 2016). Besides that, lenticular channels are related with the porosity, which is the main quality parameter for commercial value: "good cork" has few and small pores, while a "poor-quality" material has lenticular channels with a large cross-sectional area (Anjos et al., 2008).

The mechanism of the “**absorption**” mentioned before, in natural corks, could be related to processes such as diffusion in the cell walls and water penetration in the cells. First, wine (mainly composed of water) diffuses into the closed cells, as if it were permeating through the cell walls. After saturation of the cell walls by diffusion, penetration into the closed cells is the only contribution to the mass increase. The regime of penetration continues until all cells are filled (Rosa and Fortes 1993). In technical stoppers the mechanism of absorption through the pores (granulates and interstices of granules) is not yet described.

Beyond that mechanical property, there is the **rebound recovery**. A cylindrical cork when inserted into a bottle necks suffers a strain $\approx 25\text{-}30\%$ along its radial direction. For example, an initial stopper diameter of 24 mm is insert in a neck of 18 mm, which are characteristic values. In natural corks the compression almost does not affect the bulk cells and the deformation of a cork stopper occurs in a layer of thickness $\approx 25\% \theta_n$ (neck diameter), that is in the periphery, where the cells are deeply corrugated. Nevertheless, the recovery is not complete after being introduced for the first time in a bottle because a permanent deformation exists, induced whenever cork (a viscoelastic material) is deformed in the third, high-slope region of the stress-strain compression curve, and the cell walls cannot bend more due to mutual contacts (Rosa and Fortes 2009). Rosa and Fortes (1988) concluded that the recovery rate decreases appreciably with time and increases with the degree of deformation previously imposed.

The elasticity of a natural cork stopper is essentially based on the cellular structure (mainly suberin, a polymerised ester of saturated and unsaturated fatty acids which is very resistant, flexible and elastic) and on the air inclusion in a watertight, closed material (Silva et al., 2003). According to Lagorce-Tachon et al. (2016), relatively to technical corks, it seems that the size of cork particles, and ratio cork/additives, the mechanical properties matter when changing from a “cork-like” material to a “glue-like” material. However, there is no information about whether the particle size or the cork/additive ratio is the main factor impacting the mechanical properties (Jardin et al., 2015).

2.6 Wine ageing

There is a time gap between bottling and consumption of wine. This period is critical and determines the wine quality, because many changes could take place in the bottle. These “threats” include taint, oxidation and reduction. It is well known that there is a connection between the cork used and the reactions that take place in the wine (Loscos et al., 2010). A cork stopper should ensure an appropriate seal without liquid outflow and allowing wine ageing without organoleptic deterioration (Payette 2010). These risks should be well managed to prevent disastrous causes after the consumer removes the closure. The sealing performance of closures is related to their permeability properties, namely to oxygen (Saucier 2010). In fact, wine ageing is

greatly influenced by the level of oxygen that dissolves in the wine during storage. Ageing can also improve wine quality, helping to modify various organoleptic properties (Venturi et al., 2017), namely increased harmoniousness and lower harshness.

Attributes such as “honey-like”, “farm-feed”, “hay”, “woody-like” and “rotten food” are related to aged wines. Normally, red wines lose their color by spontaneous clearing, while for white wines it becomes more intense (Linsenmeier et al., 2010; McRae et al., 2015; Moreira et al., 2016). Aroma deterioration due to oxidation is often related to the synthesis of aldehydes. Aldehydes are formed by the oxidation of alcohols and volatile aldehydes increase during ageing (Rognsa et al., 2017). In contact with oxygen, acetaldehyde is one of the compounds formed. Ethanol, the most important alcohol in wine, is oxidized to acetaldehyde by a coupled auto-oxidation. A rapid oxidative spoilage was related to the presence of strong-smelling aldehydes, particularly methional and phenylacetaldehyde. The last compound is associated with “honey-like” aroma. Methional is also an important aldehyde and can be formed by the direct peroxidation of methionol to methional or by Stecker degradation (Linsenmeier et al., 2010).

Oxygen affects wine evolution (which is good) but also its deterioration (caused by oxidation). However, oxidative degradation is mainly due to oxidative reactions promoted by oxygen itself, a process dissimilar from that going on in wine aging, in which the modifications in composition are “encouraged” by various types of chemical reactions. Oxidation is one parameter that determines the shelf life and is conditioned by the wine resistance and the level of exposure to oxygen. Oxidative degradation depends also on pH, storage temperature, as well as on the presence of exogenous antioxidants (SO_2 and ascorbic acid) and others parameters (Ferreira et al., 2002; Ferreira et al., 2003; Venturi et al., 2017).

2.7 Chemical parameters

Authors such as Godden et al. (2001) reported that *“Sulfur dioxide concentration was found to be a particularly important measurement when assessing the comparative performance of closures. Small differences in mean SO_2 concentration among closures observed at an early stage were found to be strong predictors of differences in later sensory performance”*. SO_2 is used at bottling and throughout the winemaking process and has both antioxidant and antimicrobial properties. This compound protects wines by inhibiting enzymic and nonenzymic oxidation as well as preventing spoilage microorganisms (acetic acid bacteria, molds and certain wild yeasts). *Saccharomyces cerevisiae* is inhibited at 0.8 ppm of molecular SO_2 and bacteria and wild yeast at 0.4 ppm. Chemical degradation of this compound during storage represents an index of oxidative degradation as a function of the storage conditions. High levels of SO_2 perceptible upon sensory evaluation are considered a wine flaw because it can inhibit the malolactic fermentation. An

acceptable concentration of molecular level is about 0.8 ppm, but many factors have to be taken into account (Saucier 2010; Steiner 2010).

Sulphite exists in two different states in wine: free and bound. Free sulphur dioxide can take three different forms: molecular (SO_2), when in solution with water; bisulphite, when it is a HSO_3^- ion; sulphite, when it is a SO_3^{2-} ion. Bound is when these forms combine with compounds such as phenols, acetaldehyde and sugar. The free SO_2 is effectively the barrier against microbes and oxidation, while the bound SO_2 is the part which has already done its work and cannot be useful any longer in this context (Preedy 2014). Monitoring the total and free SO_2 content in wine is critical during wine storage and processing to ensure protection from chemical and microbiological agents and to obey the current legislation. The maximum level of total and free sulfur dioxide is fixed in the European Community by the International Organization of Vine and Wine (OIV) and it depends on the type of wine (up to 150 mg/L for red wines and up to 200 mg/L for white wines). (Giménez-Gómez et al., 2017).

The volatile acidity (VA) quantification also plays a significant role and a high content can be an indicator of microbiological contamination and, consequently, of the degradation of the wine (Vidigal and Rangel 2017). VA is a measure of the wine's gaseous acids (acids that can be removed by steam distillation) that contributes to the smell and taste of vinegar. Those compounds are primarily acetic acid but also lactic, formic, butyric, and propionic acids. The concentration of volatile acidity is largely caused by microbial metabolism as a byproduct. Acetic acid results from the conversion of both glucose and ethanol by acetic acid bacteria. Other sources are lactic acid bacteria and others. Aroma compounds such as ethyl acetate that usually go hand in hand with acetic acid are unpleasant and have a detection threshold between 100 and 120 mg/L, below the threshold of acetic acid, from 600 mg/L and 900 mg/L (Neeley 2004). U.S. legal limits are 1.2 g/L for red wines and 1.1 g/L in the case of white wines (Instituto da Vinha e do Vinho 2009).

2.8 Sensorial analysis

Sensorial analysis is crucial to assess the quality of a wine. In this work, it is important to highlight two sensory techniques: Duo-trio Test and Napping® with Ultra-Flash Profiling (UFP).

2.8.1 Duo-Trio Test

A Duo-Trio Test is an overall difference test which will determine whether a sensory difference exists between two samples (Lesschaeve and Noble 2010). Three samples are presented and one of them is a reference sample. Judges indicate which coded sample matches the reference. The number of correct replies is counted and the total number of responses. A table of statistical significance helps on the interpretation, according to ISO 10399:2017. There is a number that

supports a specific statistical difference, and if the correct answers are below it, the samples cannot be distinguished (Jackson 2017).

2.8.2 Napping® with Ultra-Flash Profiling (UFP)

Napping® is a method based on the idea that inter-perceived product differences can be expressed as a Euclidian configuration in a unique session (Giacalone et al., 2016; Varela and Ares 2014). This method considers the individual perception of the judges. They position all products on a blank paper of a size similar to a standard A2 sheet in a way that if the products are sensory identical, they will be very near and if they are perceived as different, they will have a certain distance among them. Hence, the judge has his/her own criteria and there are no right or wrong solutions. Each wine will have a X co-ordinate and a Y co-ordinate, which allows to collect directly a Euclidian configuration for each subject. At the end of the task, the judges write the sample code in the place they put on the sheet (Giacalone et al., 2016; Perrin et al., 2008). Data are collected using a coordinate system (the origin is normally placed in the bottom left corner) and entered a data matrix. The matrix has the columns with the information about X and Y coordinates and the rows are the products under test. A complement to Napping is the UFP, a quick descriptive procedure, which allows the addition of a list of sensory attributes that judges find appropriate to describe the samples. The data analysis is comprised two main parts: analysis of data generated during the Napping® and analysis of the descriptive outputs (Giacalone et al., 2016).

Multiple Factor Analysis (MFA) seems to be the best choice to treat the Napping data, because it allows to consider the individual criteria and relative importance of each judge. MFA is a generalization of a well-known chemometric test, principal component analysis (PCA) (Abdi and Valentin 2007), and analyses multiple sets of variables measured on the same observations. For example, the different data sets can be the wines evaluated by different subjects (different judges) or groups of subjects (each judge evaluates the wines with his/her own set of scales). The goal is to evaluate if there is an agreement between the subjects or groups of subjects (Abdi et al., 2013). In MFA each table is normalized by dividing all its elements by the first singular value of this data table. This transformation ensures that the singular value of the first principal component of each data table is equal to 1 and, therefore, that no data table can dominate the common solution only because it has a larger inertia on its first dimension. After, there is a combination of these data tables into a common representation of the observations, using a PCA. It is obtained from the concatenation of the normalized data tables. This PCA decomposes the variance of the concatenated table into a set of new principal components or factors, ordered by the amount of variance that each component explains (Abdi et al., 2013; Le Dien and Pagès 2003). After the achievement of the factor scores, these can be used to plot maps in such a way that the distances in the map best reflect the similarities/differences between the observations (Lê et al., 2015).

3 Materials and Methods

In this research, chemical, physical and sensorial evolution of a red and a white wine, stored in glass bottles (0.750 L) closed with six different cork stoppers, were evaluated over a period of twelve months. To avoid differences in the concentration of O₂, the wine collected was bottled at the same time. Consequently, the different evolution of the oxidative processes detected during time can be attributed to the different oxygen intake during storage. All bottles with suspicion of having TCA were removed from the study by expert people.

The six different closures were: VINC, VINC+, D3, D5, DNT and NATURAL. VINC, VINC+ and NATURAL belong to CSP. The others are commercial competitors, given aliases for confidential reasons. VINC, VINC+, D3, D5, DNT are technical corks. The bottles were lying down, in the dark, at room temperature.

3.1 The closures

The six different closures included in the study (with standard dimensions of approximately 44 x 24 mm) were: VINC, VINC+, D3, D5, DNT and NATURAL. VINC, VINC+ and NATURAL belong to CSP. The others are commercial competitors, given aliases for confidential reasons. VINC, VINC+, D3, D5, DNT are technical corks. Table 1 presents some characteristics of the target closures.

Table 1 - Characteristics of the six stoppers used in the project

Closures	Granule Size (mm)	Binder	Composition of cork - mean (%)	Density (kg/dm ²)
VINC	0.5 - 2.0	Polyurethane glue	>75	257 ± 7
VINC+	0.5 - 1.0	Polyurethane glue	>75	266 ± 6
DNT	1.0 - 3.0	Polyurethane glue	90*	284 ± 4
D3	0.3 - 0.8	Polyurethane glue	65*	278 ± 8
D5	0.3 - 0.8	Polyurethane glue	65*	278 ± 9
NATURAL	N.A.	N.A.	100	166 ± 22

* Values estimated based on market information and type of granules; N.A. - Not applicable.

3.2 The wine

Bottling is a complex step of the winemaking process. The implementation of good bottling practices begins with preparation adapted to the type of wine. Each wine (red and white) were produced with several grape varieties, which will influence the sensory attributes. The processes and characteristics are discriminated for red and white wines in Figure 3. Bottling occurred in March 2017.

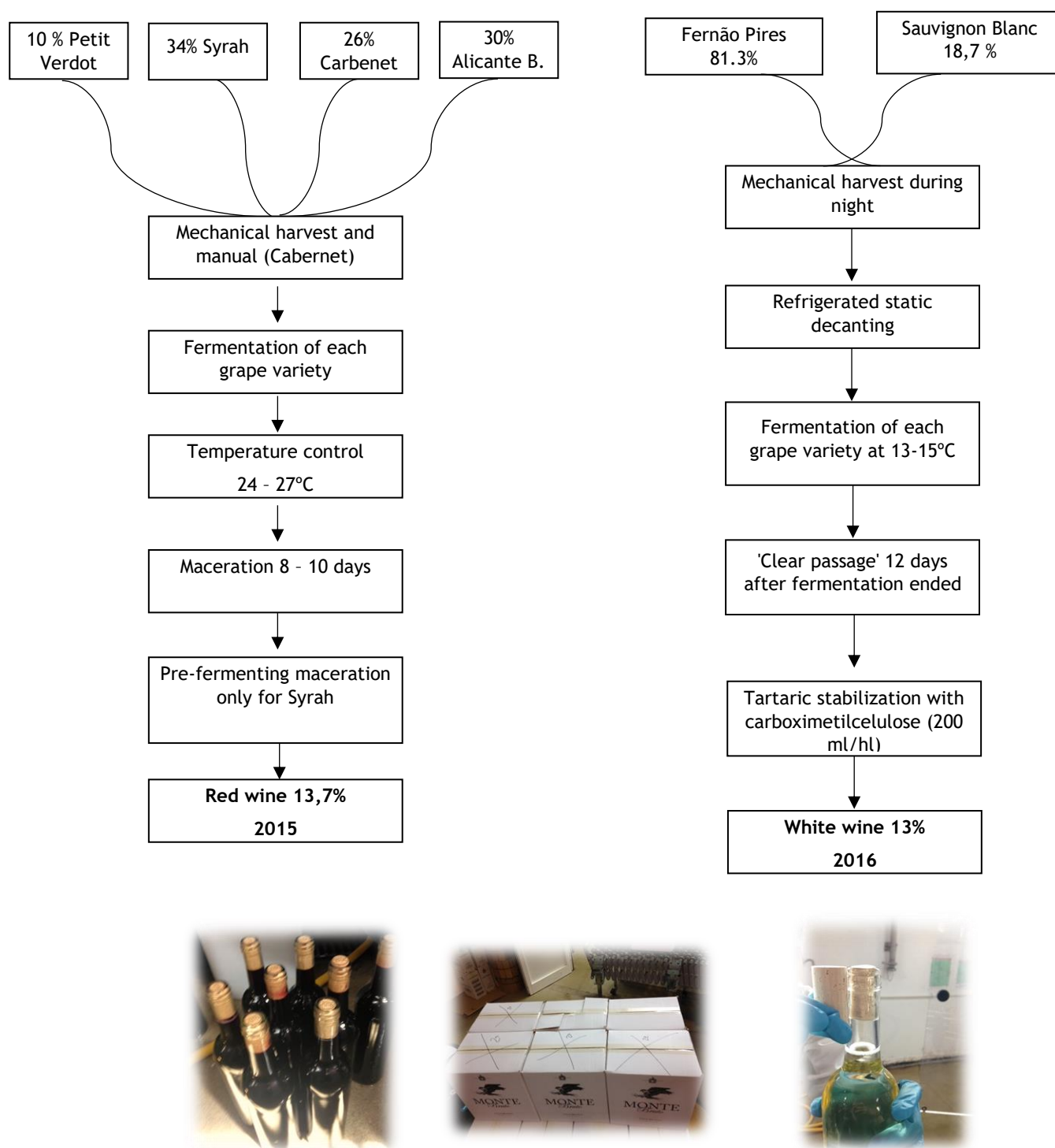


Figure 3 - Steps of the bottling process (white and red wine) in March 2017

3.3 Analytical methods

3.3.1 Physical variables

3.3.1.1 Extraction Force

The extraction force test is regulated by the ISO 9727-5:2007. The test consists of applying an extraction force in the longitudinal direction of the bottle neck, after the fixation of the cork to a pulling device and, after this, the cork stopper is pulled out (Figure 4). The device used is operated by an electric engine with a compression gauge sensor (Med TC 2000). All data were done, at least, in triplicate.



Figure 4 - Sequential steps of the of Extraction Force test

3.3.1.2 Rebound recovery

The rebound recovery test is regulated by ISO 9727-4:2007(E). This part of ISO 9727 specifies a test method for determining the percentage of diameter recovery of cylindrical cork stoppers. Measurements with a caliper occur immediately after extraction and 15 minutes after (Figure 5). The percentage of rebound recovery is the ratio of the final and initial diameters measured. All data were done, at least, in triplicate.



Figure 5 - Diameter measurements of the stoppers using a caliper, for the rebound recovery tests

3.3.1.3 Absorption

The absorption test is determined by the mass difference before and after drying the stopper for 3h at 103°C. First, the weight after cork extraction is measured. Then, all the corks are in the oven for 3h at 103°C. In order to stabilize the temperature the stoppers stay in a desiccator for 30 minutes. Finally, the stopper is weighted again. All the steps are pictured in Figure 6.



Figure 6 - Absorption test exemplified in several steps (from left to right, initial weighing, oven drying, desiccator stabilization and final weighing)

The absorption is then calculated by the ratio between the difference of initial (after extraction) and final (dry) weight and the initial weight.

3.3.2 Chemical variables

The chemical analysis of the wines (total and free SO₂ and the volatile acidity) was conducted at the accredited laboratories of the Comissão de Viticultura da Região dos Vinhos Verdes (CVRVV). The laboratory uses the OIV-AS323-04B:2009 procedure to measure total and free sulfites. OIV - AS refers to the Compendium of Analysis of International Methods of Wine and Musts. The volatile acidity is a test based on MI074, an Internal Method of CVRVV that uses the Fourier Transform infrared spectroscopy (FTIR spectroscopy).

3.3.3 Sensory analysis

For the study, 11 tasters were used. All the tasters (P1 until P11) are characterized in Table 2. Note that not all of them were present in all tests, but all the people who participated are present in the table. Next to their code are the functions that they perform.

Table 2 - Tasters used in the sensory analysis and their knowledge and expertise level

Reference	Knowledge and expertise level	
	Wine	Cork
P1	Winemaker	Sensory expert
P2	Consumer	Sales & product expert
P3	Consumer	Marketing
P4	Consumer	Sales & product expert
P5	Winemaker	End user
P6	Consumer	Sales
P7	Consumer	Sales
P8	Consumer	Product & sensory expert
P9	Winemaker	Sensory expert
P10	Consumer	Product & sensory expert
P11	Winemaker	End user

* Expert refers to more than 3 years' experience

3.3.3.1 Duo-trio

A Duo-Trio test is an overall difference test which will determine whether or not a sensory difference exists between two samples. An example of a scheme of this test is shown in Figure 7.



Figure 7 - Duo-trio sensory test scheme (wines disposed and the taster's sheet)

3.3.3.2 Napping® with UFP

In this test, the descriptors used are based on a list previously shown. The samples are arranged such that the ones a taster considers to be similar to one another are close together and the ones

that they consider to be different are further apart. Figure 8 is an example of a final result of how this test could be applied by the tasters. The codes are the different wines with different closures.

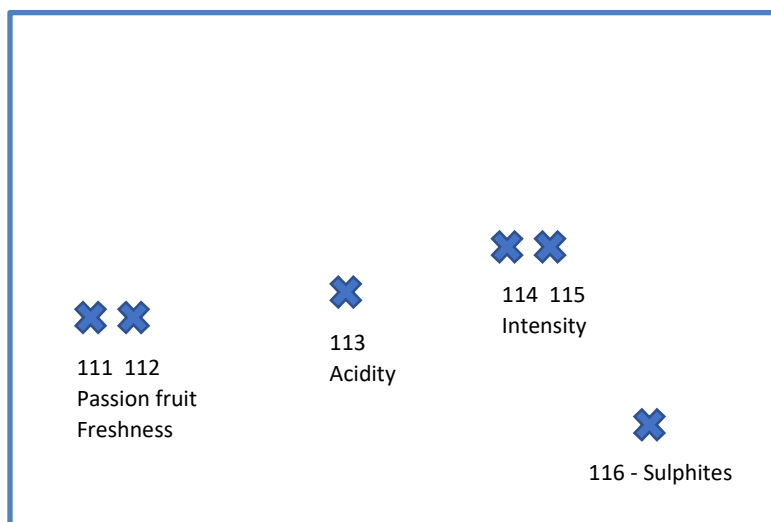


Figure 8 - Example of a Napping sheet with the codes (wines) and descriptors

3.3.3.3 Ranking

A complement is the overall score for each wine (sum of the punctuation). The quantitative scale was based on (Cicchetti and Cicchetti 2009). The scale that each taster used was: 1- objectionable; 2- acceptable; 3- pleasant; 4- good; 5- very good; 6- extraordinary.

3.4 Data analysis

All statistical analyses related with the physical variables were performed with SPSS Version 24.0 statistic software. For each parameter (extraction force, rebound recovery and absorption), mean, standard deviation (SD) and amplitude ([Min, Max]) were calculated. Taking into account all the months analyzed, a non-parametric Kruskal-Wallis test were performed. Then, concerning the last month, a Kruskal-Wallis test followed by a post-hoc Mann-Whitney U test were done to determine whether the difference between the medians of stoppers is statistically significant. To evaluate for potential correlation of all variables, non-parametric Spearman correlations were calculated. Data were considered statistically significant at $P < 0.05$.

All statistical analyses related with the Napping® data were implemented in the FactoMineR package in the free statistical software R (Lê et al., 2008). A Multiple Factor Analysis (MFA) was performed to analyze all the variables simultaneously and allowed the study of the relationship between the observations.

After Napping®, sensory judges carried out an ultra-flash profiling (UFP). In practice, they wrote some words near the position of all, or most of products. For each judge and for each wine the experimenter assigned a “1” if a descriptor was cited for the wine and a “0” if not.

It is relevant to detail the analysis: Data included, for each assessor, the coordinates for each sample placement according to a reference, where the zero point (0,0) was the lower left corner of the napping sheet. The total number of assessors were called “P1”, “P2”, “P3”, etc., and, logically, the coordinates corresponding to each judge were X1, Y1, X2, Y2, and so on. Each row of the table corresponded to one sample, so that the first column consists of the sample names. The following part of the data table consists of all assessors’ coordinates. Thus, the assessor’s X and Y coordinates were two adjacent columns for each one. Following the assessor coordinate, part of the data table was the attribute part because ultra-flash profile was performed. This part was a contingency table, meaning that each column has an attribute and the following rows correspond to the total number of occurrences of that attribute for all assessors in that wine.

All statistical analyses related with all the variables (physical, chemical and sensorial) at 12 months were further analyzed by a cluster dendrogram. It was performed with raw data, namely the mean of extraction force, rebound recovery, absorption, density, volatile acidity, free SO₂, total SO₂, sensorial and total score (ranking score). The raw data was provided, and the software automatically computed a distance matrix in the background. The distance matrix shows the distance between the six objects (closures), in each type of wine (Forina et al. 2002).

4 Results and Discussion

4.1 Closure physical measurements

The main objectives regarding all the physical measurements performed on the different cork stoppers (extraction force, rebound recovery and absorption) were: (1) realize if there were any differences/tendency for each parameter in each closure along the bottling time (Kruskal-Wallis H test); (2) notice if there were differences regarding the performance of the different closures one year after bottling (Kruskal-Wallis H test followed by a Mann-Whitney U test); (3) correlate all the variables (Spearman's rank correlation coefficient).

4.1.1 Extraction force

For all the closures, the extraction force, which corresponds to the force required to remove the closure from the bottle according to ISO 9727-5: 2007, was measured at 4, 5, 6, 8 and 12 months. This performance is related with the ease with which consumers can extract the closures from bottles. The structure of the closure has a big influence in the ease of extraction and directly affects the adhesion (friction) to the glass bottle neck (Robertson 2013).

About the first objective, during the bottling time in each closure, it is possible to see an irregularity on the behaviour, without any tendency until the twelve months (last measurement) (Figure A - 1 - Annex A). The Kruskal-Wallis (KW) test was used to compare the groups of data, in this case, all the months observed. It was possible to conclude that there was no statistically significant difference between the extraction force by different months in all closures, except for VINC+. Table 3 summarizes the extraction forces values and the results for the KW Test. Statistically significant mean differences are flagged with two asterisks (**). Authors such as Godden et al. (2001), observed a variability and inconsistent evolution in this parameter during the same storage time independently of the type of closure. Thus, this variable probably needs much more bottling time before any definite conclusion can be drawn (Godden et al., 2001).

The second objective is related with the performance among stoppers at one-year bottling. Observing the (Figure A - 1 - Annex A) it is possible to detect that a clear difference among two groups of closures exist in that last measurement: the highest values (in daN) include D3 (34.3), D5 (31.5), VINC (30.8) and the lowest one including NATURAL (24.8), VINC+ (23.7) and DNT (22.4). There was a statistically significant difference in the last measurement by different closures ($H(5) = 25.991$, $p < 0.01$). A Post hoc comparison using the Mann-Whitney U test was conducted to compare them.

Table 3 - Extraction forces (daN) for the six closures along the bottling time

	VINC	VINC+	D3	D5	NATURAL	DNT
Months	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD
4	26.6 $\pm$ 8.2	22.6 $\pm$ 2.4	35.1 $\pm$ 2.3	34.8 $\pm$ 2.2	23.1 $\pm$ 4.6	24.5 $\pm$ 2.0
5	33.8 $\pm$ 2.2	26.8 $\pm$ 4.6	34.2 $\pm$ 0.6	34.7 $\pm$ 4.4	22.0 $\pm$ 2.9	26.0 $\pm$ 5.0
6	30.0 $\pm$ 10.8	30.4 $\pm$ 6.8	31.5 $\pm$ 5.3	35.1 $\pm$ 3.6	25.8 $\pm$ 3.4	29.5 $\pm$ 6.8
8	33.5 $\pm$ 19.8	31.3 $\pm$ 8.8	33.2 $\pm$ 2.5	31.1 $\pm$ 7.1	24.7 $\pm$ 3.7	24.3 $\pm$ 8.2
12	30.8 $\pm$ 6.7	23.7 $\pm$ 8.8	34.3 $\pm$ 2.1	31.5 $\pm$ 4.0	24.8 $\pm$ 7.3	22.4 $\pm$ 6.5
Total	29.4 $\pm$ 9.3	25.0 $\pm$ 6.6	34.2 $\pm$ 2.9	33.6 $\pm$ 3.8	23.9 $\pm$ 5.2	24.6 $\pm$ 5.3
[Min, Max]	[14.0, 55.4]	[12.4, 42.8]	[22.0, 38.8]	[21.9, 39.4]	[14.3, 41.5]	[12.6, 37.5]
Kruskal Wallis Test	H(4)=5.443, p=0.245	H(4)=11.887, p=0.018**	H(4)=4.257, p=0.372	H(4)=7.181, p=0.127	H(4)=2.679, p=0.613	H(3)=3.710, p=0.295

** Sig < 0.05

Hence, with Mann-Whitney U test (Table A - 1 - Annex A) was possible to conclude that: within each “group” mentioned above the p-value is greater than the significance level (5%), so there are not enough evidences to conclude that the difference between the population medians is statistically significant; comparing stoppers belonging to different groups, the p-value is less than or equal to the significance level, so the decision is to reject the null hypothesis and accomplish a difference between the population medians that is statistically significant. The larger variability (standard error) and the wider amplitude of measurements correspond to VINC [14.0, 55.4] and VINC+ [12.4, 42.8].

One of the reasons for these differences may be related with the treatment of the closure surface that is critical to improve the sealant properties and the removal from bottleneck. In fact, this lubrication treatment, which reduces the friction, facilitates the insertion/extraction from the bottle (Giunchi et al., 2008).

4.1.2 Rebound recovery

The rebound recovery was measured at the same time as the extraction force, that is, at 4, 5, 6, 8 and 12 months (Table 4). This parameter is important because it is related with the closure elasticity with the long-time of storage of bottled wine. The theoretical optimum value is 100%, meaning that the closure could return exactly to its initial dimension.

Observing Figure A - 2 - Annex A and considering the performance of each closure along the bottling time, it is again impossible to visualize a tendency and the KW test proved no statistically significant difference for the rebound recovery between the different months in all closures.

Comparing the performance among the stoppers at the twelfth month (Table A - 2 - Annex A), no statistically significant difference was detected between closures ($H(5) = 5.930$, $p > 0.05$), so there is not enough evidence to reject the null hypothesis that the group medians are all equal. Thus, this property does not distinguish the behaviour of the closures after one year of bottling.

Table 4 - Rebound recoveries (%) for the six closures along the bottling time

	VINC	VINC+	D3	D5	NATURAL	DNT
Months	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD
4	83.7 $\pm$ 1.0	83.4 $\pm$ 1.0	83.9 $\pm$ 1.2	83.3 $\pm$ 0.9	82.7 $\pm$ 1.1	84.6 $\pm$ 1.0
5	82.1 $\pm$ 1.0	82.3 $\pm$ 1.8	82.5 $\pm$ 1.5	83.1 $\pm$ 2.2	82.6 $\pm$ 1.4	84.0 $\pm$ 1.0
6	82.8 $\pm$ 1.2	83.8 $\pm$ 1.4	82.8 $\pm$ 1.5	83.1 $\pm$ 1.6	83.0 $\pm$ 0.8	83.5 $\pm$ 1.1
8	82.4 $\pm$ 0.6	83.6 $\pm$ 0.7	82.3 $\pm$ 0.3	83.4 $\pm$ 0.5	82.0 $\pm$ 0.8	82.8 $\pm$ 0.9
12	80.7 $\pm$ 0.3	81.7 $\pm$ 1.0	82.5 $\pm$ 0.7	81.5 $\pm$ 0.7	80.9 $\pm$ 0.8	81.9 $\pm$ 0.8
Total	83.0 $\pm$ 1.5	83.4 $\pm$ 1.5	83.6 $\pm$ 1.7	83.6 $\pm$ 2.1	82.8 $\pm$ 1.6	84.1 $\pm$ 1.5
[Min, Max]	[80.3, 85.8]	[80.4, 85.6]	[80.1, 86.8]	[80.2, 85.4]	[80.0, 84.6]	[80.9, 86.5]
Kruskal Wallis Test	H(4)=8.505, p=0.075	H(4)=1.912, p=0.752	H(4)=8.322, p=0.080	H(4)=0.229, p=0.994	H(4)=1.852, p=0.763	H(3)=6.928, p=0.074

4.1.3 Absorption

Although absorption could have some different meanings regarding all the tests made in cork stoppers, in this case it is a parameter that measures the difference between the weight of the closure after it was plugged out from the bottle and after a subsequent three hours drying process at 103 °C.

Contrary to the parameters mentioned before, a tendency started to show as time went on, as seen in Figure A - 3 - Annex A. Table 5 summarizes the absorption values and the results for the KW Test. It was possible to conclude that there was a statistically significant difference between the absorption by different months in all closures, except for NATURAL.

There was a statistically significant difference in the last measurement by different closures ($H(5) = 58.707$, $p < 0.01$). A Post hoc comparisons using the Mann-Whitney U test (Table A - 3 - Annex A) was used to relate them. The test indicated that the absorption was not significantly higher for VINC than for VINC+, $U=62.0$, $p=0.564$, whereby there are no evidences to conclude that the difference between the medians is statistically significantly. All the other combinations were significantly different.

Detailing the interpretation for each of the stoppers, NATURAL has the highest values (asthmatically different from all the others); VINC, VINC + and DNT have a very similar pattern, with an apparent tendency to increase on a non-linear trend; D3 and D5 present a pattern similar to each other, presenting a saturation level at the end of one year. However, continuous studies with a wider time span are to be considered for confirmation; D5 always has the lowest values along the time scale.

Overall, the differences between NATURAL corks and the technical ones could be due to their differences in composition. Technical corks are made of a much more hydrophobic material. Lagorce-Tachon et al. (2016) state that the presence of additional components to cork such as glue or polymer micro-sphere used in agglomerated stoppers, slightly reduces the water sorption capacity. Then, the changes observed could be in line with the hydrophobic character of the additives used, for example, polyurethane adhesive and micro-spheres of poly(acrylonitrile). Also, this corroborates with the findings of Godden et al. (2001) that affirmed that technical corks were found to be more “watertight” than the natural corks.

Table 5 - Absorption values (%) for the six closures along the bottling time

	VINC	VINC+	D3	D5	NATURAL	DNT
Months	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD
4	7.42 $\pm$ 1.06	6.92 $\pm$ 0.53	6.24 $\pm$ 0.36	5.74 $\pm$ 0.22	9.69 $\pm$ 1.55	7.38 $\pm$ 0.16
5	8.88 $\pm$ 0.42	7.36 $\pm$ 0.24	7.23 $\pm$ 0.42	6.51 $\pm$ 0.09	11.11 $\pm$ 3.11	8.00 $\pm$ 0.20
6	8.89 $\pm$ 0.97	8.61 $\pm$ 1.47	7.44 $\pm$ 0.30	6.91 $\pm$ 0.33	10.37 $\pm$ 1.27	8.42 $\pm$ 0.21
8	8.47 $\pm$ 0.12	7.91 $\pm$ 0.23	7.44 $\pm$ 0.19	7.18 $\pm$ 0.27	10.39 $\pm$ 0.42	8.68 $\pm$ 0.25
12	8.64 $\pm$ 0.71	8.42 $\pm$ 0.68	7.47 $\pm$ 0.30	6.95 $\pm$ 0.48	12.60 $\pm$ 3.13	9.37 $\pm$ 0.33
Total	8.15 $\pm$ 1.07	7.66 $\pm$ 1.01	6.91 $\pm$ 0.68	6.38 $\pm$ 0.68	10.74 $\pm$ 2.43	8.22 $\pm$ 0.90
[Min, Max]	[6.69, 11.58]	[6.19, 11.48]	[5.87, 8.03]	[5.42, 7.70]	[7.84, 17.57]	[7.17, 9.82]
Kruskal Wallis Test	H(4)=21.347, p=0.001**	H(4)=23.494, p=0.001**	H(4)=26.248, p=0.001**	H(4)=29.891, p=0.001**	H(4)=4.943, p=0.293	H(3)=28.269, p=0.001**

** Sig < 0.05

4.1.4 Relationship between all the variables

In order to achieve more conclusive outcomes, the Spearman's rho test was used to relate extraction force, rebound recovery and absorption among themselves two by two. Like all correlation coefficients, this test measures the strength of association of two variables in a single value between -1 and +1. Table 6 summarizes the results obtained.

Table 6 - Spearman's rank correlation coefficient based on physical measurements for the six cork stoppers

Spearman's rho	Extraction Force	Extraction Force	Rebound Recovery
	Rebound Recovery	Absorption	Absorption
VINC	-0.32*	0.19	-0.61**
VINC+	0.23	0.12	-0.11
D3	-0.14	-0.24	-0.58**
D5	0.33*	-0.39*	-0.36*
NATURAL	0.07	0.01	-0.37*
DNT	0.22	0.01	-0.68**

*The correlation is significant at the 0.05 level (bilateral); ** The correlation is significant at the 0.01 level (bilateral).

As Pereira (2007) mentioned, a relation between extraction force and absorption was expected because the impregnation with wine influences the extraction force of stoppers, reducing the effort to uncork bottles. Nevertheless, during the first year of bottling this link was not so relevant.

Observing Table 6, a negative correlation was found between rebound recovery and absorption, which was statistically significant for closures such as VINC, D3, D5, NATURAL and DNT. This relationship could be explained by the phenomenon of diffusion along the cork. As the pores are getting more filled with wine, by mechanisms such as diffusion in the cell walls and wine penetration in the cells, the absorption is higher which makes fewer pores available for the air to fill them. Thus, there will probably be less capacity for expansion (and, consequently, lowest percentage of rebound recovery). However, it is important to underline that technical corks have less percentage of cork, reducing the capacity of absorption as mentioned in section 4.1.3.

4.2 Wine composition

4.2.1 Sulfur dioxide measurements

The following images (Figure 9-12) represent the total and free SO_2 data for white and red wine during one year of bottling with observations every 4 months.

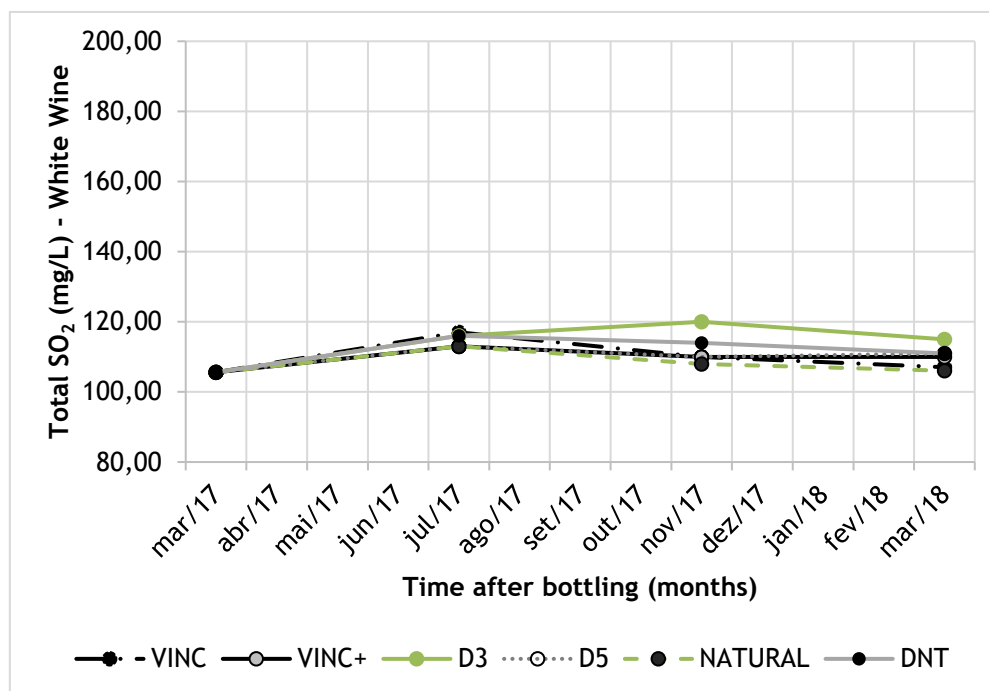


Figure 9 - Concentration of total SO_2 in bottles sealed with each closure type over time in white wine

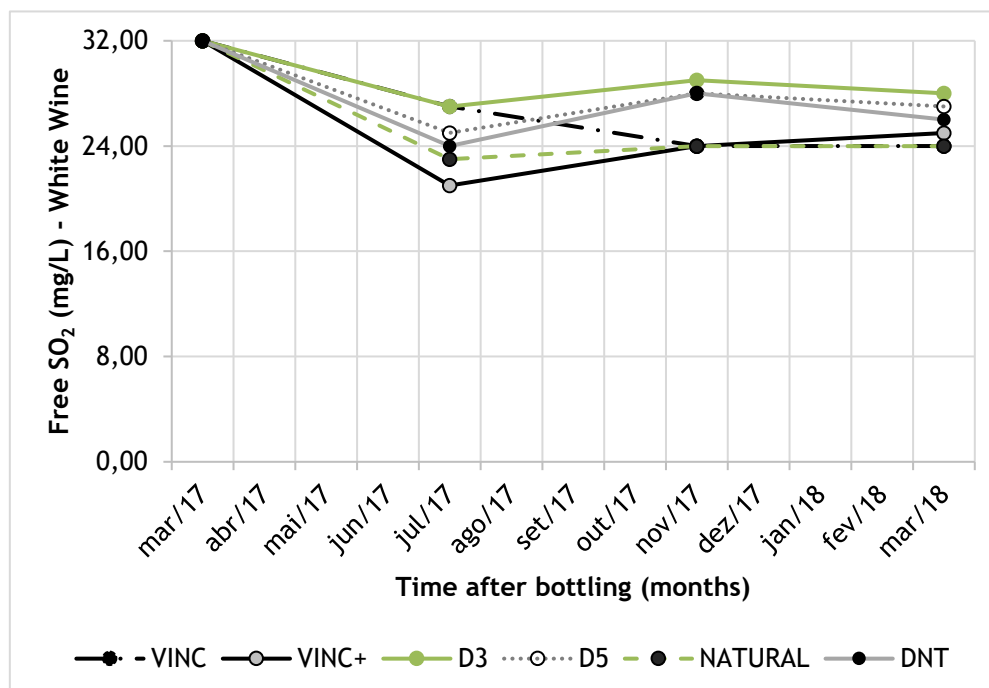


Figure 10 - Concentration of free SO_2 in bottles sealed with each closure type over time in white wine

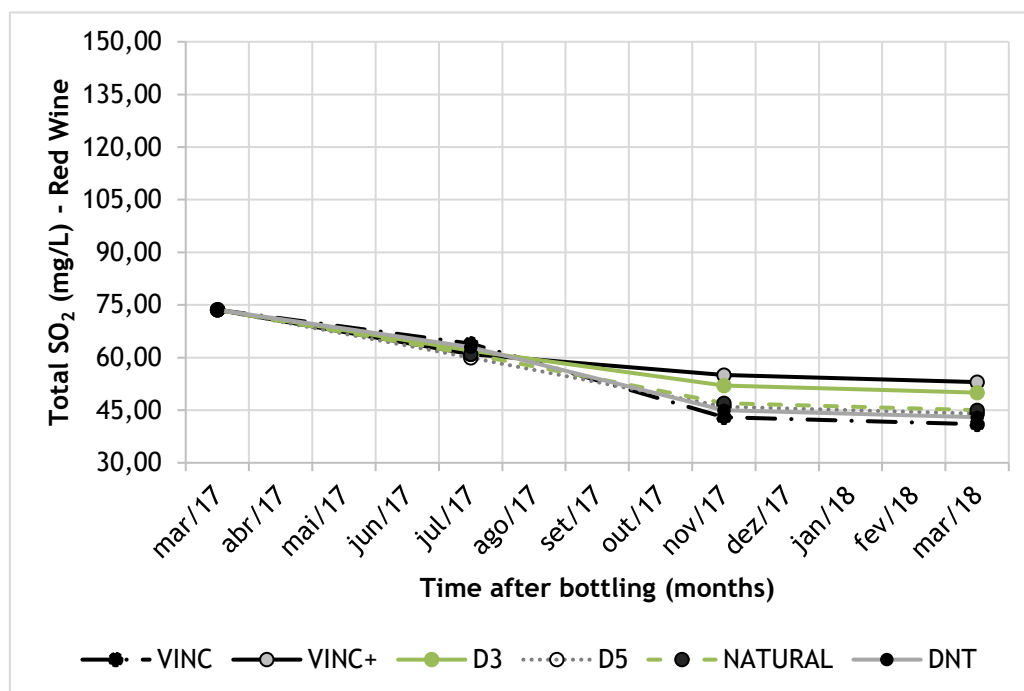


Figure 11 - Concentration of total SO_2 in bottles sealed with each closure type over time in red wine

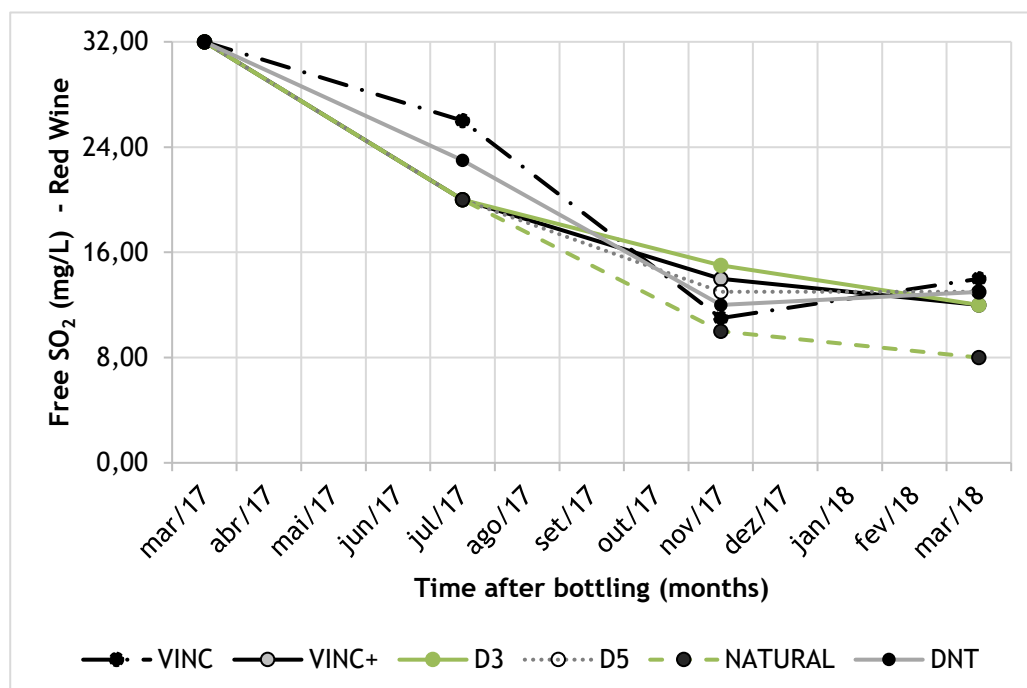


Figure 12 - Concentration of free SO_2 in bottles sealed with each closure type over time in red wine

Firstly, the differences between total and free content of SO_2 in white wine (Figures 9 and 10) and in red wine (Figures 11 and 12) are clear. The objective of the information on the sulfurous content is essential since it acts as antioxidant, ensuring protection against chemical and microbiological agents. Due to factors beyond our control, in the months represented in the graphs, only one analysis per wine with a different stopper was performed. Thus, any statistical treatment is pointless. The scales of the graphs agree with the maximum level allowed in Portugal/EU, that is 150 mg/L in red wines and 200 mg/L in white wines for total SO_2 .

In white wine (Figure 9) an almost constant evolution is observed bearing in mind the error of the method itself being around 10%. In addition, it is not possible to confirm differences between wines with different corks compared to this parameter, which is not surprising considering the year bottling time. In the case of free SO_2 (Figure 10) there is a small decrease in the first four months, which remains approximately constant. It should be noted that the method error is around 25% (according to the report issued by CVRVV), so the differences between values are still within the range of possible errors.

In red wine (Figure 11) there was a steeper decrease at the end of the 12 months when compared to white wine, but apparently without significant differences between wines with different stoppers. Also, free SO_2 shows a marked decrease when compared to white, and after 12 months, the NATURAL stopper presents the minimum necessary limit of free SO_2 to be effective in its function (8 mg/L). All other corks have identical behaviors. However, it is based only in one bottle that, for some reason, could be in worst storage conditions.

It would be interesting to verify if some reactions occurred over time and if this decrease is due to a high oxidation, studying oxidative markers that would likely give more information. It seems that, in this case, red wine has had a stronger oxidation over time (higher loss of free SO_2) when comparing to white wine. Authors such as Godden et al. (2001) verified that there was a trend for wine sealed with the technical cork closures to retain SO_2 better than wine sealed with natural cork but this was only particularly evident after 18 months. One year could be a short time in terms of SO_2 retention. Despite these sensory tests did not reveal relevant oxidation notes.

4.2.2 Volatile acidity measurements

As can be seen in Figures 13 and 14, the volatile acidity remains approximately constant during the storage and the small variations that occur are within the errors values of the analytical method. Thus, this parameter only shows that the values are far from the maximum legal values, 1.2 g/L for red wines and 1.1 g/L for white wines (Instituto da Vinha e do Vinho 2009).

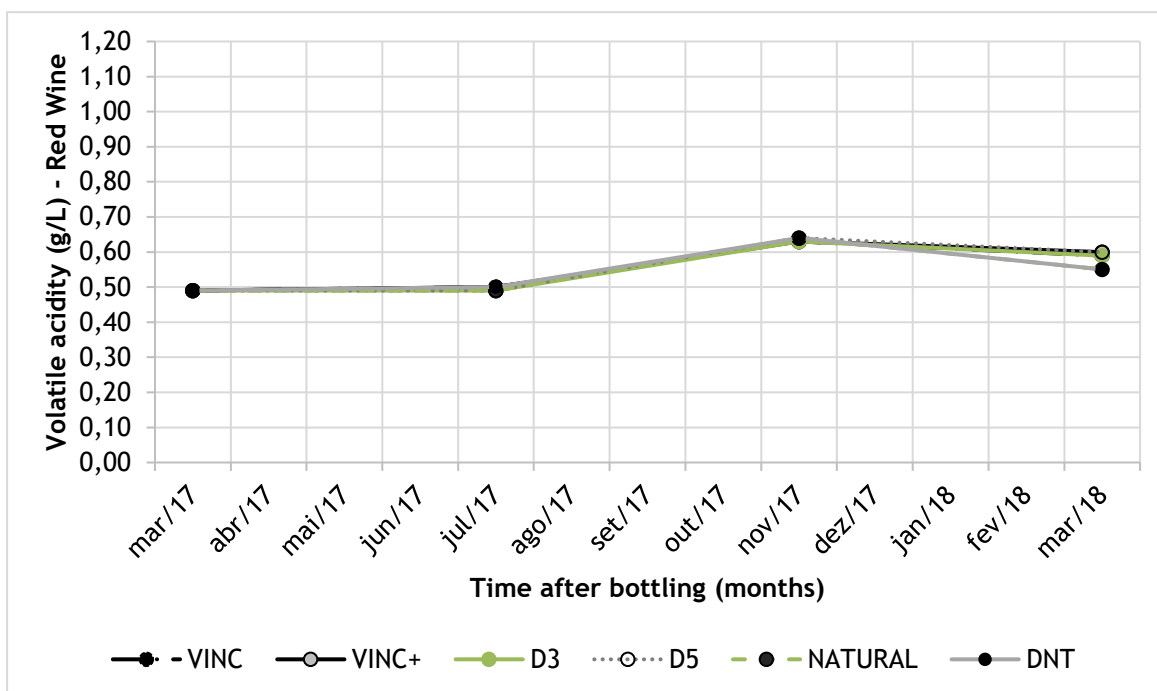


Figure 13 - Concentration of volatile acidity in red wine for one year

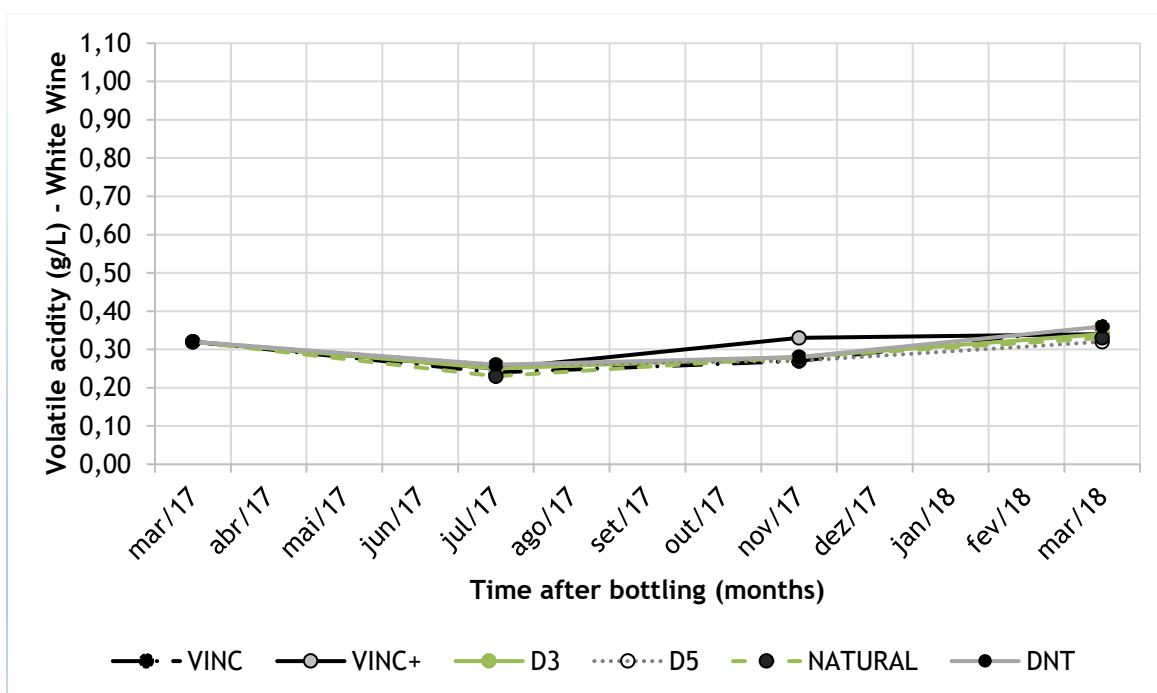


Figure 14 - Concentration of volatile acidity in white wine for one year

4.3 Wine sensory analysis

4.3.1 Five months testing

In August, 5 months after bottling, a duo-trio and a preference test were done (Figure 15). There were eight judges, two of them winemakers and the other six wine consumers. A duo-trio test was obtained to answer if there were differences between VINC+, D5 and between VINC, D3, based on market positioning of the closures. Each judge received a set of 4 groups of 3 samples (one labelled as the reference and two labelled with different codes). The assessors indicated which of the coded samples believed to be the same as the reference. Therefore, in all tests the number of correct responses were not sufficient to conclude that the two products were perceptibly different, $\alpha=0,05$ (statistical significance at 95%).



Figure 15 - Presentation of a duo-trio test

The preference test revealed that, for white wine, all judges had difficulties to choose his/her preference. A common commentary was about D5, because it tended to “lower” the character of the wine for a while. In red wine D3 was the less preferred because of intense vegetable notes.

From this point on, we began to apply other sensory techniques because forcing groups that were supposed to happen could lead to gross errors in the end.

4.3.2 Eight months testing

At eight months, the Napping sensory technique was used and supplemented with the Ultra-Flash Profiling (UFP). The descriptors (previously chosen by a team of specialized people) characterized each type of wine (white and red). Varietal characteristics and others related to the evolution of wine were included. The judges could use all of the descriptors or just the ones that they could distinguish in the samples. Figure 16 shows an example of a wine tasting session.

The tasters were asked to place the samples according to their own criteria. In the case of white wine, the descriptors were: freshness, passion fruit, woody, citric, acidity, apricot, reduction, oxidation and chemical character. For red wine the descriptors were: vegetable, tannins, fruity, chemical character, chocolate, woody, floral, cherry, reduction and oxidation. For descriptors

such as oxidation, chemical and woody character, standards were provided. Thus, the data analysis comprised two main parts: data generated during the Napping® and descriptive outputs.



Figure 16 - Wine tasting in CSP1

4.3.2.1 White Wine

The bottles used in the white wine tests are shown in Figure 17. The analysis performed comprised the sample places generated using Napping® data, reflected in the graph type “Individual factor map” (Figure 18). The individual factor map has all the wines displayed and the position of each one in the global analysis is the barycenter of their positions for the 9 judges and taking account their descriptors.



Figure 17 - Bottles used in wine tasting with the different stoppers of white wine

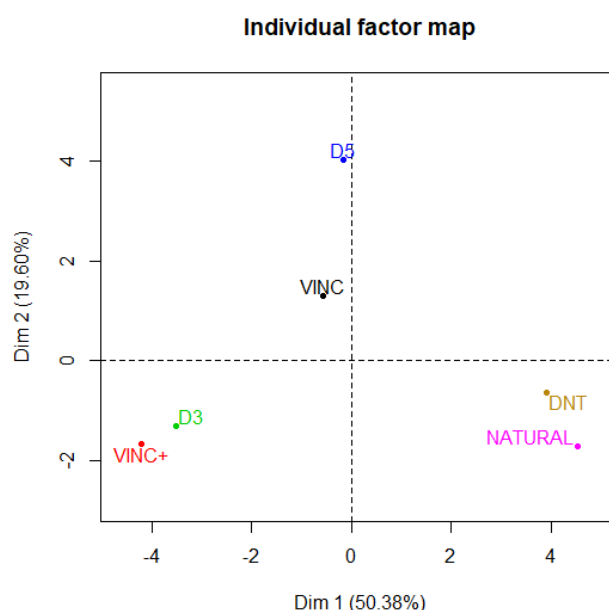


Figure 18 - Individual factor map related to white wine at 8 months

In the white wines, the first component has an eigenvalue equal to 11.04, which corresponds to 50.38 % of the total inertia. The second component, with an eigenvalue of 4.29, explains 19.60% of the inertia (Figure B - 1 - Annex B). The first two axes accounted for about 70% of the total inertia and will be kept for the analysis, even the third axis has a percentage of explained variance similar to the second one. Authors such as Giménez-Gómez et al. (2017) state that 70 % is a quite good variance in sensorial analysis.

The first axis opposed the wines with NATURAL cork stoppers (which contributed alone to 31% of the axis construction) and DNT (which contributed to 23%) to the others, particularly to VINC+ and D3 (together they contributed an amount of 45% of the axis) (Table B - 1 - Annex B). The second axis opposed wine with D5 stopper (with a contribution of 63%) to the others. The relative distances from the wines is a point to take into consideration and, as can be seen in Figure 18, there are essentially 3 groups that are formed: VINC+ and D3, D5 and VINC, DNT and NATURAL. Initially, these groups were not expected to be formed, since at a commercial level, as mentioned in section 4.3.1, it was expected that VINC +; D5 and VINC; D3 could be together. Napping® came to show that the groups that had initially been used in the Duo-Trio should not be forced.

Figure 19 shows which variables influenced the most the position of the wines. In dimension 1 these were taster P2 (wine consumer; sales & product expert in cork sector) and P9 (winemaker and sensory expert in cork sector) and the descriptors “reduction” and “chemical character”. In dimension 2, taster P3 (wine consumer and belonged to marketing cork sector) has a higher preponderance. Wine consumers usually have less knowledge than the winemakers, and this could bias the MFA distribution.

Most of the groups have close coordinates on the first dimension which means that their contribution to the first principal component is quite the same. It also means that the first principal component of the MFA is common to most of the variables.

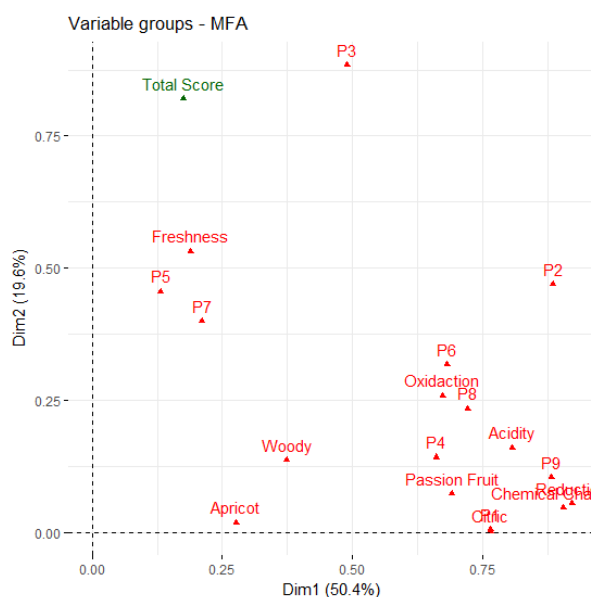


Figure 19 - Variables grouped according to the individual factor map for white wine at 8 months

In order to better understand which descriptors were associated with the different wines, a PCA was performed with only those descriptors (Figure 20). The explained variance on the first axis is 63.8% and in the second axis is 17.1%.

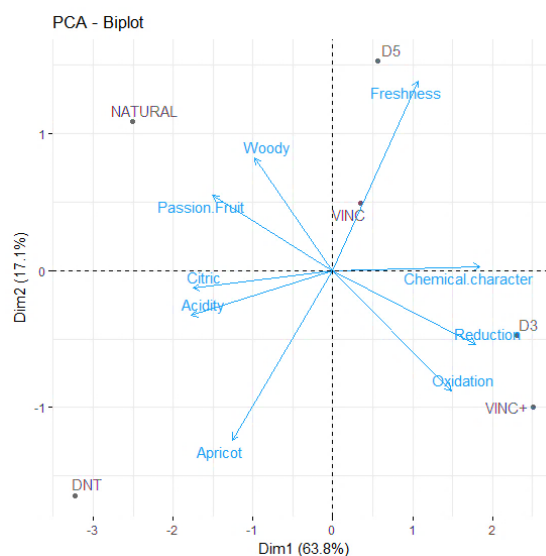


Figure 20 - PCA (Biplot of groups and samples) for white wine at 8 months

Figure 20 shows that D5 is associated to “freshness”, whereas D3 and VINC + are associated to the “reduction” and “oxidation” descriptors, respectively. Wine with NATURAL cork is related to “passion fruit” and “woody” descriptors. Regarding the way the descriptors are related, “reduction” and “oxidation” are in the same quadrant when they should be perceived as opposites,

so it can be concluded that the tasters used them in the same way, which would not be predictable.

A supplementary group was included in the MFA: Total Score (presented in a green color in Figure 19). This group did not have any impact on the global configuration but was included as superimposed variables. This supplementary variable was applied in order to add information on the scatter plots for a better understanding of the data. Total score is the result of a ranking procedure. Each taster gave the wines between 1 and 6 points. Total score is the sum of all punctuations from the tasters.

From Table 7 it is clear that D5 is most highly ranked (27.5), followed by VINC (22.5). The lowest score was for VINC+ with 16.5. These results come to an agreement of the correspondent descriptors. D5 is related with the “freshness” and VINC+ with “oxidation”.

Table 7 - Total score of white wines at 8 months in descending order of punctuation

Total score	
27.5	D5
22.5	VINC
21.5	DNT
20.5	NATURAL
17	D3
16.5	VINC+

As can be seen in Figure 19, “Total Score” is positioned at the top of the dimension 2, which makes sense because there is a distinction of D5 (contributed most by axis 2) from the others.

4.3.2.2 Red Wine

The same sensorial method (Napping® with UFP) was used for red wines (Figure 21). The same standard was provided for descriptors “oxidation”, “chemical” and “woody character”.



Figure 21 - Bottles used in wine tasting with the different stoppers of red wine

In MFA (Figure 22) the first component has an eigenvalue equal to 8.43, which corresponds to 40.51 % of the total inertia and the second component, with an eigenvalue of 5.66, explains 27.16% (Figure B - 2 - Annex - B). Thus, the first two components accounted for about 68% of the total, a satisfactory percentage. Regarding the individual factor map, there is a differentiation of D3 and VINC +; D5; VINC; NATURAL and DNT. The groups (D3, VINC+) and (NATURAL, DNT) were also formed in the white wine, what was particularly curious and was kept in mind during the following tests. The first axis opposed the wines VINC+ (which contributed alone to 33% of the axis construction) and DNT (which contributed to 27%) in opposite sites, to the others (Table B - 2 - Annex - B). The second axis opposed the wine VINC, with a contribution of 51%, to the others.

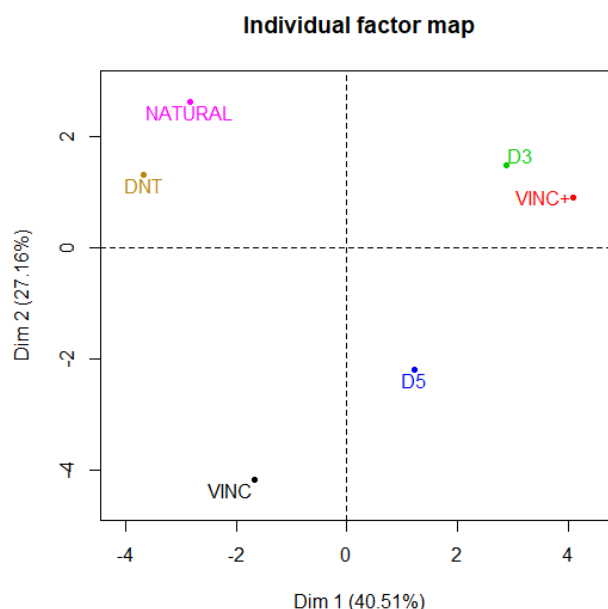


Figure 22 - Individual factor map related to red wine at 8 months

The graph of the MFA variable groups (Figure 23) proves that in dimension 1 tasters P2 (wine consumer; sales & product expert in cork sector) and P7 (wine consumer, belonged to sales in cork

In Figure 24 wines are presented organized with their descriptors. Wine with NATURAL cork is associated with the “Cherry” descriptor, while D3 is associated to “woody”. VINC has a connection with “fruity” and “tannins”; DNT with “reduction” and VINC+ with “vegetal”.

Total score is represented in Table 8. Wine with the NATURAL closure ranks highest (32.5), followed by VINC (29). The worst places are for D3 (22) and VINC+ (23), like in the case of the white wine. Figure 22 also shows a distinction between the stoppers mentioned above (NATURAL; VINC and VINC+; D3).

Table 8 - Total score of red wines at 8 months in descending order of punctuation

Total score	
32.5	NATURAL
29	VINC
27	D5
27	DNT
23	VINC+
22	D3

4.3.3 Twelve months testing

The same procedure was done 4 months after, i.e., at the final of one year of bottling, using the same different closures. The results are presented below.

4.3.3.1 White Wine

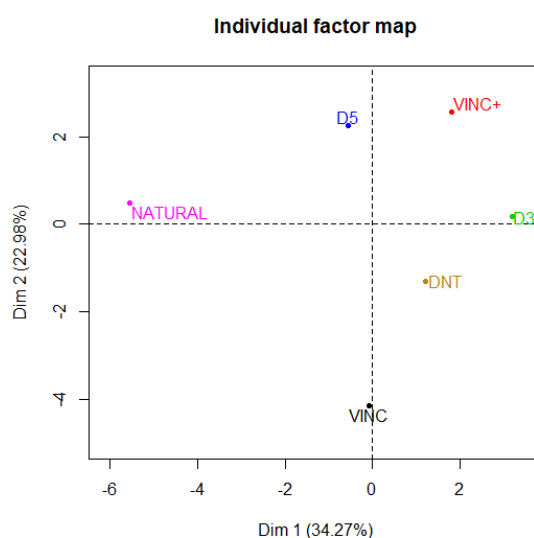


Figure 25 - Individual factor map related to white wine at 12 months

The first component has an eigenvalue equal to 7.66, which corresponds to 34.27 % of the total inertia and the second component, with an eigenvalue of 5.14, explains 22.98%. The first two components accounted for about 57% of the total, what is less than the total inertia at 8 months (70%). The first axis (described in Figure 25) opposed the wine with NATURAL stopper (which contributed to 67% of the axis construction) to the others. The second axis opposed the wine with the VINC closure to the others, with a contribution of 56% (Figure B - 3 Annex - B). Instead of forming different groups like at 8 months, a major difference started to appear between NATURAL and all the other technical stoppers.

The variable groups for white wine at 12 months (Figure B - 4 Annex - B) demonstrate that in dimension 1, taster P5 and descriptor “woody” influenced the most, while in dimension 2 taster P9 had the highest influence, followed by descriptor “citric” and taster P2. The tasters were kept to have a comparison term, and again, the influence of P2 and P9 is high-pitched. In later studies this should be taken into account.

In Figure 26 wines are presented together with their descriptors. Wine with NATURAL cork is related to “woody” character, as 4 months before, suggesting a character similar to the “cork odor”, since NATURAL has obviously the highest percentage of cork comparing to the others. D5 was associated to the “freshness” descriptor, and at 12 months is partly related to “passion fruit”. VINC+ presents descriptors such as “citric” and “freshness”.

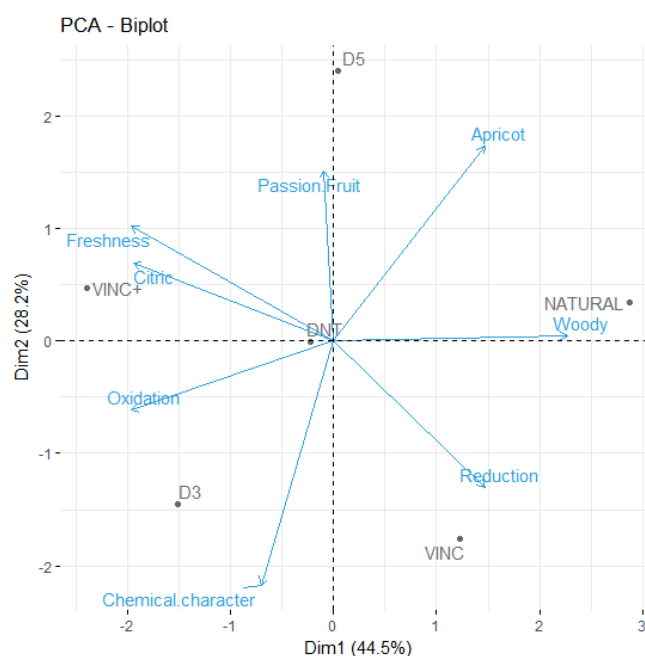


Figure 26 - PCA (Biplot of groups and samples) for white wine at 12 months

Total Score results presented in Table 9 show that D5 is ranks highest (50), followed by DNT (44). The lowest punctuation is for NATURAL (35). Since "woody" is considered an "off-flavor" it was expected that the score for this wine would also be very low.

Table 9 - Total score of white wines at 12 months in descending order of punctuation

Total score	
50	D5
44	DNT
42	D3
41	VINC+
37	VINC
35	NATURAL

4.3.3.2 Red Wine

In this case, the first component has an eigenvalue equal to 7.66, which corresponds to 35.74 % of the total inertia and the second component, with an eigenvalue of 5.14, explains 22.98%. The first two components accounted for about 63% of the total, which is again less than the total inertia at 8 months (70%). The first axis (described in Figure 27) opposed the wine with NATURAL stopper (contributed to 67% of the axis construction) to the technical corks. The second axis opposed the wine with the VINC closure to the others, with a contribution of 56%.

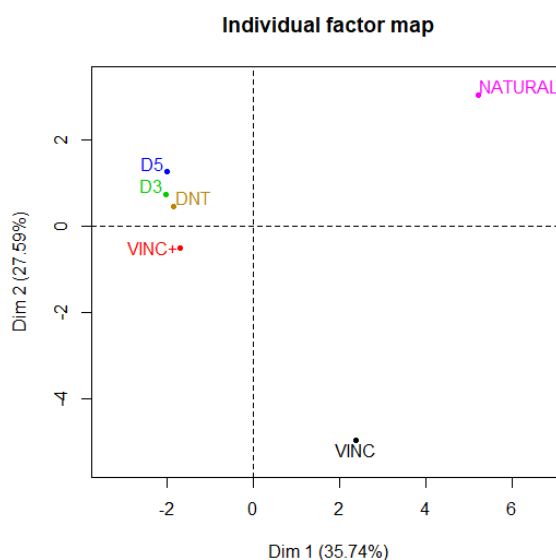


Figure 27 - Individual factor map related to red wine at 12 months

In Figure 28 wines are organized with their descriptors. Wine with NATURAL cork is associated with the “cherry” descriptor. VINC has a connection with “reduction” and “oxidation”.

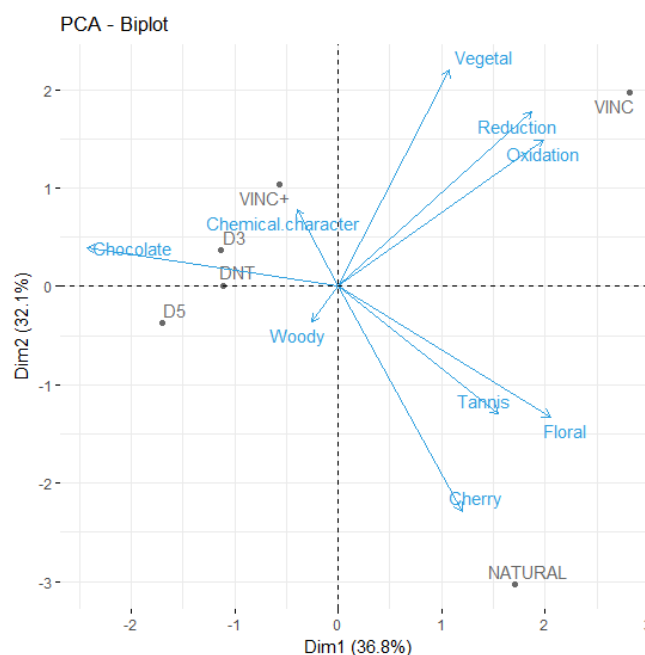


Figure 28 - PCA (Biplot of groups and samples) for red wine at 12 months

Table 10 shows that is clear that wine NATURAL has the highest rank (48), followed by D3 (43.5), with VINC in the last place with 33.

Table 10 - Total score of red wines at 12 months in descending order of punctuation

Total score	
48	NATURAL
43.5	D3
39.5	DNT
37.5	VINC+
35	D5
33	VINC

Overall, checking all sensory results, it is observed that the initial formation of small groups disappears over time (from 8 to 12 months) and a clear distinction between the natural stopper and the rest begins. The off-flavors (chemical character, oxidation and reduction) are appearing associated with different wines (with different corks), which leads to believe that there is still no clear validation of wine degradation, which would be expected because one year of bottling is a short time. The ranking shows that in white wine the D5 always presents the highest score and in

red wine the natural presents the highest score in the two test times, however the distance between scores is not yet considerable to be pronounced clearly.

Napping has already shown that the positioning between wines is effective in the intended objective, to know how the VINC and VINC+ position themselves among all the other. The two CSP corks have different behaviors over time.

4.4 Relationship of sensory data with wine compositional and closure physical data at 12 months

To assess the impact of all data (physical, compositional and sensorial) in the final arrangement of the different closures, an algorithm in R that joins similar objects into groups called *clusters* (*hierarchical cluster analysis*) was implemented (Forina et al. 2002).

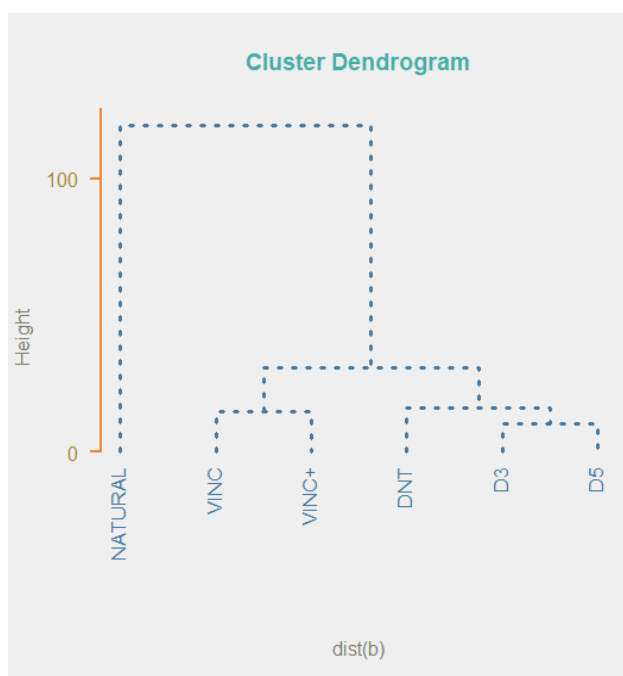


Figure 29 - Cluster dendrogram at one-year bottling in white wine

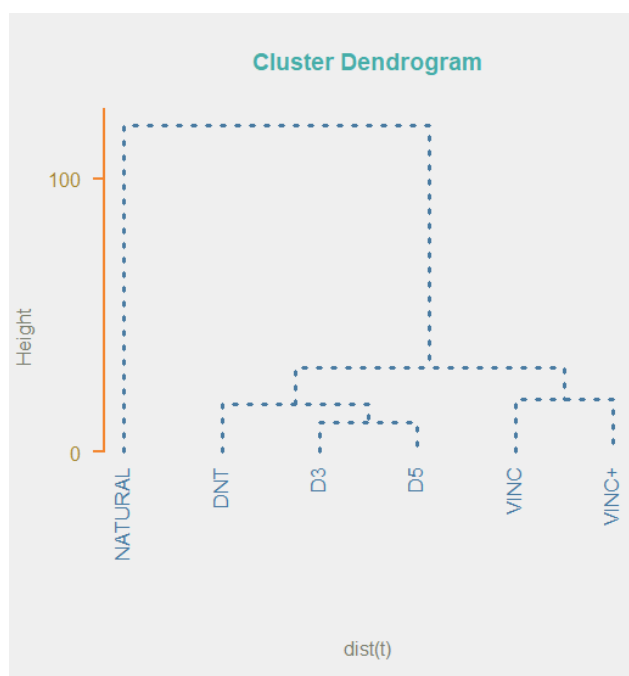


Figure 30 - Cluster dendrogram at one-year bottling in red wine

Results are expressed as a dendrogram, which is a branching diagram that represents the hierarchical relationships. The arrangement of the clades tells us which leaves (representing the different closures) are most similar to each other. Central to all of the goals of cluster analysis is the notion of degree of similarity (or dissimilarity) between the individual objects being clustered: the greater the height, the greater the difference. It is important to emphasize that the ordinate

is the similarity between groups and the abscissa has no specific meaning, but it is used only to separate the clusters.

Analyzing the results for white wine in Figure 29, it is possible to observe D3 and D5 have the highest correlation because highly correlated clusters are nearer the bottom of the dendrogram. The second highest correlation is between VINC and VINC+. DNT is more similar to D3 and D5. As we move up the dendrogram, the compound clusters get bigger and the distance between compound clusters increases in value, which means NATURAL is far away from the others (height greater than 100), even is more similar to DNT, followed by VINC and VINC+, and finally to D3 and D5. Red wine, in Figure 30, presented a similar cluster dendrogram, where D3 and D5 are the closest ones. DNT is more similar to D3 and D5 than VINC and VINC+. VINC and VINC+ are also close to each other. NATURAL shows a big distance from all others, which is reflected in a height over 100.

At first it was expected that the performance could group the cork stoppers in a different way, specifically DNT, D3 with VINC, D5 with VINC+ and NATURAL. The predict disposition (Figure 31) was based on their shelf-life. However, Figures 29 and 30 reveal that at one-year bottling there is a tendency towards a differentiation based on the cork/additive rate. The ratio cork/additives are 65% for D3 and D5, higher than 75% for VINC+ and VINC, 90% for DNT and 100% in NATURAL (Section 3.1 - The closures). Besides that, independently the type of wine, the disposition is the same.

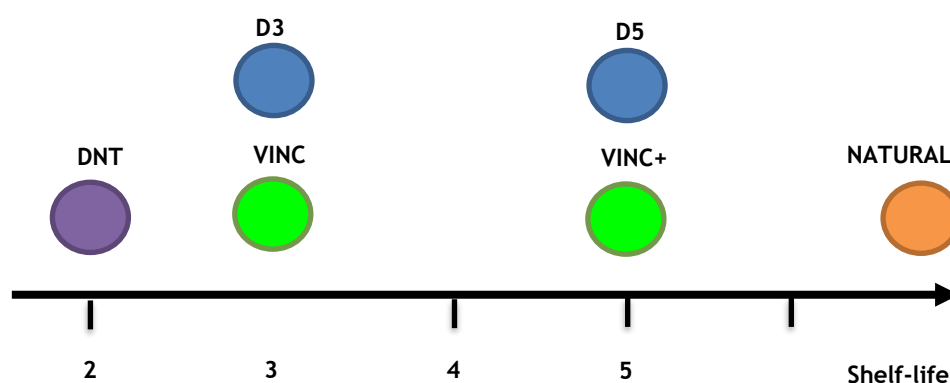


Figure 31 - Positioning of all stoppers regarding their shelf-life

5 Conclusions

The purpose of this Thesis was to comprehend the long-term effects on wine ageing using different closures (natural corks and technical stoppers - stoppers with granules and additives such as glue). Two of those technical stoppers, VINC and VINC+, are products from CorkSupply (the company where the current study took place) and are in proof. Afterwards, the performance of the closures was compared until the end of the first year of bottling, taking into account all the evaluations carried out (physical, chemical composition and sensorial).

In order to better understand the sealing properties of stoppers over time different influential factors regarding closure physical measurements were evaluated. One of the tests was the extraction force that does not disclose a tendency during the time of the study. There are also no significant differences in rebound recovery among the closures at 12 months, and nothing can be concluded in the light of the evolution of this parameter for each stopper. Absorption is the parameter that has shown the most differences. There is a tendency for stoppers' values to become steadily higher over time. The major differences are between NATURAL corks and the others, technical ones, which may be directly related to their composition. The natural cork has more cork with less hydrophobicity compared to the others, which have other additives. It should be noted that the assessment is limited to this phase of bottle conservation (one year) and could present some differences from now on.

From an inspection of the pair-wise Pearson correlation coefficient it was found that there was a moderate, negative correlation between rebound recovery and absorption, which was statistically significant for 5/6 closures. This relationship can be explained by the phenomenon of diffusion of air along the stopper. Such speculation certainly needs to be tested by appropriate experiments designed to investigate this hypothesis.

The concentrations of free SO₂, total SO₂ and volatile acidity were monitored in wine with the interest in assessing the development of bottled wine over time and, after 12 months, the levels of those parameters denote a good state of wine conservation. Wine sealed with both natural and technical closures was found to have performed similarly in terms of SO₂ retention and in the concentration of volatile acidity during the first 12 months of bottling.

From the sensory analysis carried out is evident a detachment between the natural stopper and the others also described the physical measurements. D5 in white wine was the highest ranked at 8 and 12 months as well as NATURAL in red wine had the best punctuation in the 2 moments of wine tasting. At 8 months D5 is described as “freshness” and at 12 months is partly related to “passion fruit” and the NATURAL, in all observations, is related with the descriptor “cherry”.

The Napping® tool made it possible to visualize some distinction between the VINC and VINC+ stoppers compared to the others in the study, which would not be possible with other techniques. This distinction is even more evident when, using all the data, a hierarchical relationship is established. Once again there is a great distance from the NATURAL stopper, but there is an apparent tendency for the stoppers to position themselves considering their percentage of cork. D3 and D5 have the highest correlation and are further apart from VINC and VINC+. DNT is hieratically more similar to D3 and D5. Therefore, it will be essential to pursue the studies to analyze if the “cork-like” behavior will continue. The project goes on beyond the timeline this Thesis, in search of a finer placement of the CSP stoppers among all alternatives tested. The methods used have been validated and the company is equipped with the tools for the continuity of work.

6 Evaluation of the work

Limitations and Further Work

The main limitation of this project was the temporal range of the results because it is essential to continue the study for at least another year to try to sort out the differences between cork stoppers clearly. In addition, the chemical analyzes should be done, at least, in triplicates to have statistically significant data.

For future work, it would be interesting to test the wine itself, in addition to the chemical analyzes previously decided. A complementary study of oxidative markers would allow structuring the degradation information over time and, in turn, give information about the stopper, since the oxidation of wine is directly related to the amount of oxygen that passes through the cork to the wine. Phenols are chemical compounds found in alcohol that contribute to the body and structure of the wine and which oxidize as long as the wine ages. In this case, it would be necessary to validate a method and choose some compounds to monitor over time.

Besides that, factors such as hue and intensity could be added to provide more information about the quality of the wine. Wine Color Intensity is a summation of absorbance measurements (A) in the violet, green and red areas of the visible spectrum ($A_{420} + A_{520} + A_{620}$), where A_{λ} represents the absorbance at wavelength λ . Wine Hue is a ratio of the absorbance in the violet to the absorbance in the green (A_{420}/A_{520}). In regard to color, a white wine may begin to look more gold than green as it ages and a red wine appears more brown. Once such data existed it would be interesting to correlate it with free and total SO_2 concentrations.

A deeper characterization of the stoppers could also be made, by performing image analysis using computed tomography (CT) or other related tools, regarding the characterization of the total internal and external structure of cork stoppers. Consequently, the relationship rebound recovery and absorption could be more thoroughly explained.

Lastly, with all this information, the stoppers can be positioned to face the changes in wine aging, and the company can make decisions in their global process if they wish to distance themselves or approach other cork stoppers.

References

- Abdi, H., Valenti, D. Multiple Factor Analysis (MFA). In *Encyclopedia of Measurement and Statistics*, N.J. Salkind (ed.), Thousand Oaks (CA): Sage, California, 2007, pp. 657-663
- Abdi, H., Williams, L.J., Valentin, D. Multiple factor analysis: principal component analysis for multitable and multiblock data sets. *Wiley Interdisciplinary Reviews: Computational Statistics*, **5**, 149-179 (2013).
- Anjos, O., Pereira, H., Rosa, M.E. Effect of quality, porosity and density on the compression properties of cork. *Holz als Roh-und Werkstoff*, **66**, 295-301 (2008).
- APCOR. (2017a). Entrevista a CorkSupply. <https://www.apcor.pt/entrevista-cork-supply-portugal/> (last accessed on 07-12-17)
- APCOR. (2017b). Technical Guide - Cork Stoppers.
- Bussiness Journal. (2017). Cork Supply releases VINC technical corks. <http://www.northbaybusinessjournal.com/northbay/solanocounty/6580282-181/cork-supply-vinc-technical-tca-taint> (last accessed on 02-05-18)
- Cicchetti, D.V., Cicchetti A.F. Wine rating scales: Assessing their utility for producers, consumers, and oenologic researchers. *International Journal of Wine Research*, **1**, 73-83 (2009).
- CorkSupply. (2017a). O Nosso Compromisso. <https://www.corksupply.pt/pt/a-nossa-empresa/o-nosso-compromisso/> (last accessed on 26-10-17)
- CorkSupply. (2017b). Vapex. <https://www.corksupply.com.au/au/commitment-to-quality/vapex/> (last accessed on 15-05-18)
- Culleré, L., Cacho, J., Ferreira, V. Comparative study of the aromatic profile of different kinds of wine cork stoppers. *Food Chemistry*, **112**, 381-387 (2009).
- Ferreira, A., Hogg, T., Pinho, P. Identification of key odorants related to the typical aroma of oxidation-spoiled white wines. *Journal of Agricultural and Food Chemistry*, **51**, 1377-1381 (2003).
- Ferreira, A., Pinho, P., Rodrigues, P., Hogg, T. Kinetics of oxidative degradation of white wines and how they are affected by selected technological parameters. *Journal of Agricultural and Food Chemistry*, **50**, 5919-5924 (2002).
- Forina, M., Armanino, C., Raggio V. Clustering with dendrograms on interpretation variables. *Analytica Chimica Acta*, **454**, 13-19 (2002).
- Giacalone, D., Ribeiro, L. M., Frøst, M.B. Perception and description of premium beers by panels with different degrees of product expertise. *Beverages*, **2**, 5-16 (2016).

- Giménez-Gómez, P., Gutiérrez-Capitán, M., Puig-Pujol, A., Capdevila, F., Muñoz, S., Tobeña, A., Miró, A., Jiménez-Jorquera, C. Analysis of free and total sulfur dioxide in wine by using a gas-diffusion analytical system with pH detection. *Food Chemistry*, **228**, 518-525 (2017).
- Giunchi, A., Versari A., Parpinello G.P., Galassi S. Analysis of mechanical properties of cork stoppers and synthetic closures used for wine bottling. *Journal of Food Engineering*, **88**, 576-580 (2008).
- Godden, P., Francis, L., Field, J., Gishen, M., Coulter, A., Valente, P., HOJ, P., Robison, E. Wine bottle closures: physical characteristics and effect on composition and sensory properties of a Semillon wine 1. Performance up to 20 months post-bottling. *Australian Journal of Grape and Wine Research*, **7**, 64-105 (2001).
- Instituto da Vinha e do Vinho. (2009). Limites analíticos e limites de emprego de certas substâncias em vinhos, bebidas espirituosas e vinagre de vinho. <http://www.ivv.gov.pt/np4/89/> (last accessed on 28-05-18)
- ISO 9727-5:2007. Cylindrical cork stoppers – Physical tests – Part 5: Determination of extraction force. First edition, Geneva, Switzerland (2007)
- ISO 10399:2017. Sensory analysis - Methodology - Duo-trio Test. Second edition, Geneva, Switzerland (2017)
- Jackson, R.S. *Wine Tasting - A Professional Handbook*. Academic Press, Cambridge, 2017
- Jardin, R.T., Fernandes, F.A.O., Pereira, A.B., Alves de Sousa, R.J. Static and dynamic mechanical response of different cork agglomerates. *Materials and Design*, **68**, 121-126 (2015).
- Juanola, R., Guerrero, L., Subirà, D., Salvadó, V., Insa, S., Regueiro, J.A., Anticó, E. Relationship between sensory and instrumental analysis of 2,4,6-trichloroanisole in wine and cork stoppers. *Analytica Chimica Acta*, **513**, 291-297 (2004).
- Jung, R., Schaefer, V. Reducing cork taint in wine. In *Managing wine quality*, A. G. Reynolds (ed.), Woodhead Publishing in Food Science, Technology and Science, Cambridge, 2010, pp. 387-417.
- Lagorce-Tachon, A., Karbowiak, T., Champion, D., Gougeon, R.D., Bellat, J.P. How does hydration affect the mechanical properties of wine stoppers? *Journal of Materials Science*, **51**, 4227-4237 (2016).
- Lagorce-Tachon, A., Karbowiak, T., Champion, D., Gougeon, R.D., Bellat, J.P., Mechanical properties of cork: Effect of hydration. *Materials and Design*, **82**, 148-154 (2015).
- Lagorce-Tachon, A., Karbowiak, T., Loupiac, C., Gaudry, A., Ott, F., Alba-Simionesco, C., Gougeon, R.D., Alcantara, V., Mannes, D., Kaestner, A., Lehmann, E., Bellat, J.P. The cork viewed from the inside. *Journal of Food Engineering*, **149**, 214-221 (2015).

- Le Dien, S., Pagès, J. Hierarchical Multiple Factor Analysis: application to the comparison of sensory profiles. *Food Quality and Preference*, **14**, 397-403 (2003).
- Lê, S., Josse, J., Husson, F. FactoMineR: An R Package for Multivariate Analysis. *Journal of Statistical Software*, **25**, 1-18 (2008).
- Lê, S., Lê, T.M., Cadoret, M. Napping and sorted Napping as a sensory profiling technique. In *Rapid Sensory Profiling Techniques and Related Methods*, M. Rogeaux (ed.), Woodhead Publishing in Food Science, Technology and Science, Cambridge, 2015, pp. 197-213.
- Lesschaeve, I., Noble, A.C. Sensory analysis of wine. In *Managing wine quality*, A. G. Reynolds (ed.), Woodhead Publishing in Food Science, Technology and Science, Cambridge, 2010, pp. 189-217.
- Linsenmeier, W., Rauhut, D., Sponholz, R. Ageing and flavour deterioration in wine. In *Managing wine quality*, A. G. Reynolds (ed.), Woodhead Publishing in Food Science, Technology and Science, Cambridge, 2010, pp. 459-493.
- Lopes, P., Roseira, I., Cabral, M., Saucier, C., Darriet, P., Teissedre, P.L., Dubourdieu, D. Impact of different closures on intrinsic sensory wine quality and consumer preferences. *Wine & Viticulture Journal*, **27**, 34-41 (2012).
- Loscos, N., Hernández-Orte, P., Cacho, J., Ferreira, V. Evolution of the aroma composition of wines supplemented with grape flavour precursors from different varieties during accelerated wine ageing. *Food Chemistry*, **120**, 205-216 (2010).
- McRae, J.M., Day, M.P., Bindon, K.A., Kassara, S., Schmidt, S.A., Schulkin, A., Kolouchova, R., Smith, P.A. Effect of early oxygen exposure on red wine colour and tannins. *Tetrahedron*, **71**, 3131-3137 (2015).
- Moreira, N., Lopes, P., Ferreira, H., Cabral, M., Guedes de Pinho, P. Influence of packaging and aging on the red wine volatile composition and sensory attributes. *Food Packaging and Shelf Life*, **8**, 14-23 (2016).
- Observador. (2016). Construir a rolha perfeita - CorkSupply. <http://observador.pt/2016/02/02/construir-rolha-perfeita-cork-supply-portugal/> (last accessed on 06-12-17)
- Oliveira, V., Knapic, S., Pereira, H. Classification modeling based on surface porosity for the grading of natural cork stoppers for quality wines. *Food and Bioprocesses*, **93**, 69-76 (2015).

- Oliveira, V., Lopes, P., Cabral, M., Pereira H. Influence of cork defects in the oxygen ingress through wine stoppers: Insights with X-ray tomography. *Journal of Food Engineering*, **165**, 66-73 (2015).
- Olivella, M. A., Caixach, J., Planas, C., Oliveras, A., Jové, P. Concentrations of organochlorine pesticides and 2,4,6-trichloroanisole in cork bark. *Chemosphere*, **86**, 754-758 (2012).
- Payette, T. J. Particular wine quality issues. In *Winemaking Problems Solved*, C. Butzke (ed.), Woodhead Publishing in Food Science, Technology and Science, Cambridge, 2010, pp. 345-386.
- Pereira, H. *Cork: Biology, Production and Uses*. Elsevier Science, Oxford, 2007
- Perrin, L., Symoneaux, R., Maître, I., Asselin, C., Jourion, F., Pagès, J. Comparison of three sensory methods for use with the Napping® procedure: Case of ten wines from Loire valley. *Food Quality and Preference*, **19**, 1-11 (2008).
- Preedy, V.R. *Processing and impact on antioxidants in beverages*. Elsevier Science, Oxford, 2014
- Robertson, G.L. *Food Packaging - Principles and Practice*. Taylor and Francis Group, U.S.A, 2013
- Rognså, G. H., Rathe, M., Petersen, M.A., Misie, K.E., Hersleth, M., Morten, S., Jens, R. From wine to wine reduction: Sensory and chemical aspects. *International Journal of Gastronomy and Food Science*, **9**, 62-74 (2017).
- Rosa, M.E., Fortes, M.A. Rate effects on the compression and recovery of dimensions of cork. *Journal of Materials Science*, **23**, 879-885 (1988).
- Rosa, M.E., Fortes, M.A. Recovery of used cork stoppers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **344**, 97-100 (2009).
- Rosa, M.E., Fortes, M.A. Water Absorption By Cork. *Wood and Fiber Science*, **25**, 339-348 (1993).
- Santos, P.T., Pinto, S., Marques P.A.A.P., Pereira, A.B., Alves de Sousa, R.J. Agglomerated cork: A way to tailor its mechanical properties. *Composite Structures*, **178**, 277-287 (2017).
- Saucier, C. How do wine polyphenols evolve during wine ageing? *Cerevisia*, **35**, 11-15 (2010).
- Silva, A., Lambri, M., Marco, D.F. Evaluation of the performances of synthetic and cork stoppers up to 24 months post-bottling. *European Food Research and Technology*, **216**, 529-534 (2003).
- Steiner, T.E. Wine packaging and storage. In *Winemaking Problems Solved*, C. Butzke (ed.), Woodhead Publishing in Food Science, Technology and Science, Cambridge, 2010, pp. 150-198.
- Tarasov, A., Rauhut, D., Jung, R. "Cork taint" responsible compounds. Determination of haloanisoles and halophenols in cork matrix: A review. *Talanta*, **175**, 82-92 (2017).
- Varela, P., Ares, G. *Novel techniques in sensory characterization and consumer profiling*. Taylor and Francis Group, U.S.A, 2014

Venturi, F., Sanmartin, C., Taglieri, I., Xiaoguo, Y., Quartacci, M.F., Sgherri, C., Andrich, G., Zinnai, A. A kinetic approach to describe the time evolution of red wine as a function of packaging conditions adopted: Influence of closure and storage position. *Food Packaging and Shelf Life*, **13**, 44-48 (2017).

Vidigal, S., Rangel, A. A flow-based platform for measuring the acidity parameters in wine. *Talanta*, **168**, 313-319 (2017).

Waterhouse Lab. (2004). Volatile acidity. <http://waterhouse.ucdavis.edu/whats-in-wine/volatile-acidity> (last accessed on 06-06-18)

Annex A - Data of Closure Physical Measurements

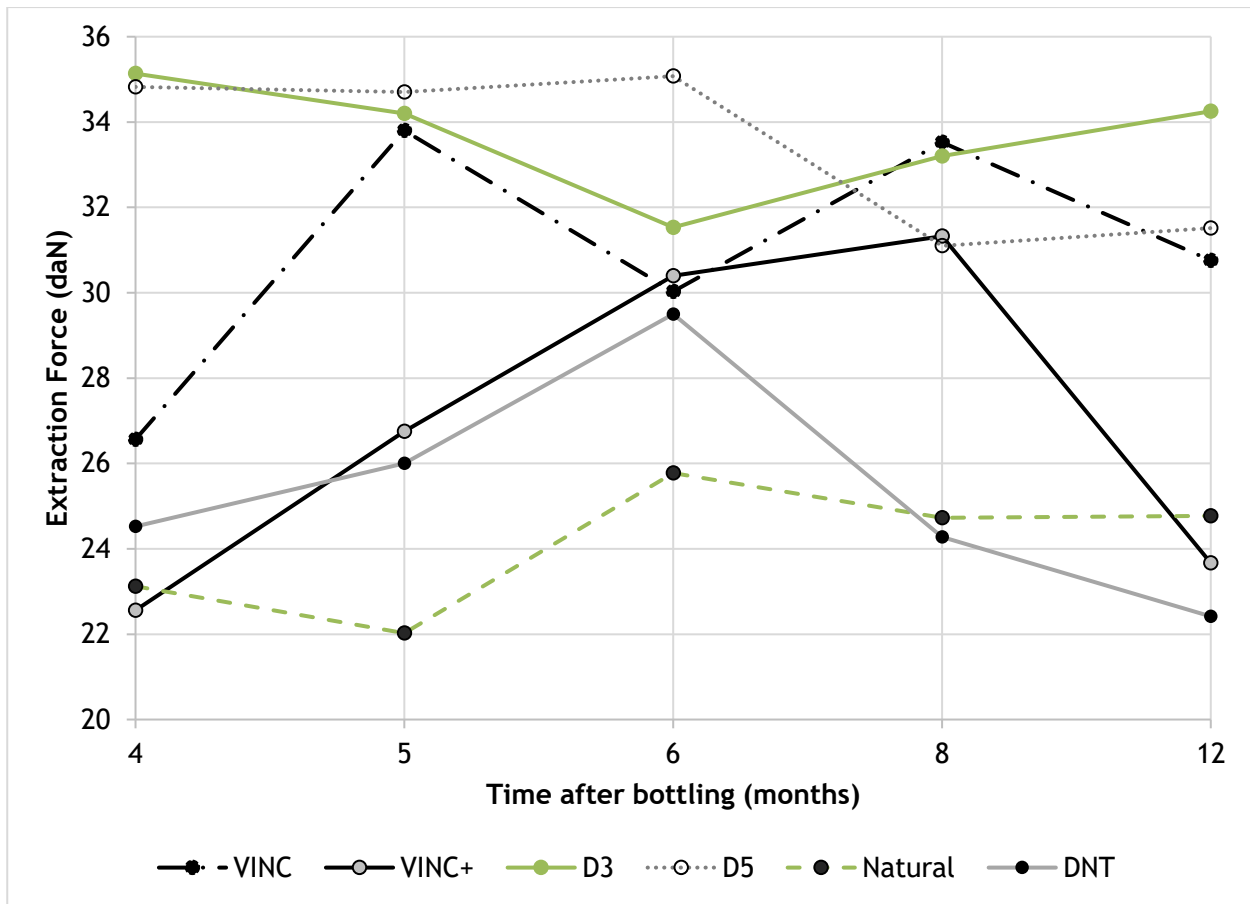


Figure A - 1 - Extraction force during one year of bottling regarding all closures

Table A - 1 - Results of U Mann-Whitney for extraction force at 12 months

	VINC VINC+	VINC D3	VINC D5	VINC NAT	VINC DNT	VINC+ D3	VINC+ D5	VINC+ NAT	VINC+ DNT	D3 D5	D3 NAT	D3 DNT	D5 NAT	D5 DNT	NAT DNT
U Mann-Whitney	37.0	58.0	70.5	38.0	27.0	25.5	34.5	63.0	71.0	39.5	14.0	2.0	25.0	13.0	57.0
Z	-2.0	-0.8	-0.1	-2.0	-2.6	-2.7	-2.2	-0.5	-0.1	-1.9	-3.3	-4.0	-2.7	-3.4	-0.9
Sig.	0.04	0.42	0.93	0.05	0.01	0.01	0.03	0.60	0.95	0.06	0.00	0.00	0.01	0.00	0.39

* Orange shading are the values with sig> 0.05

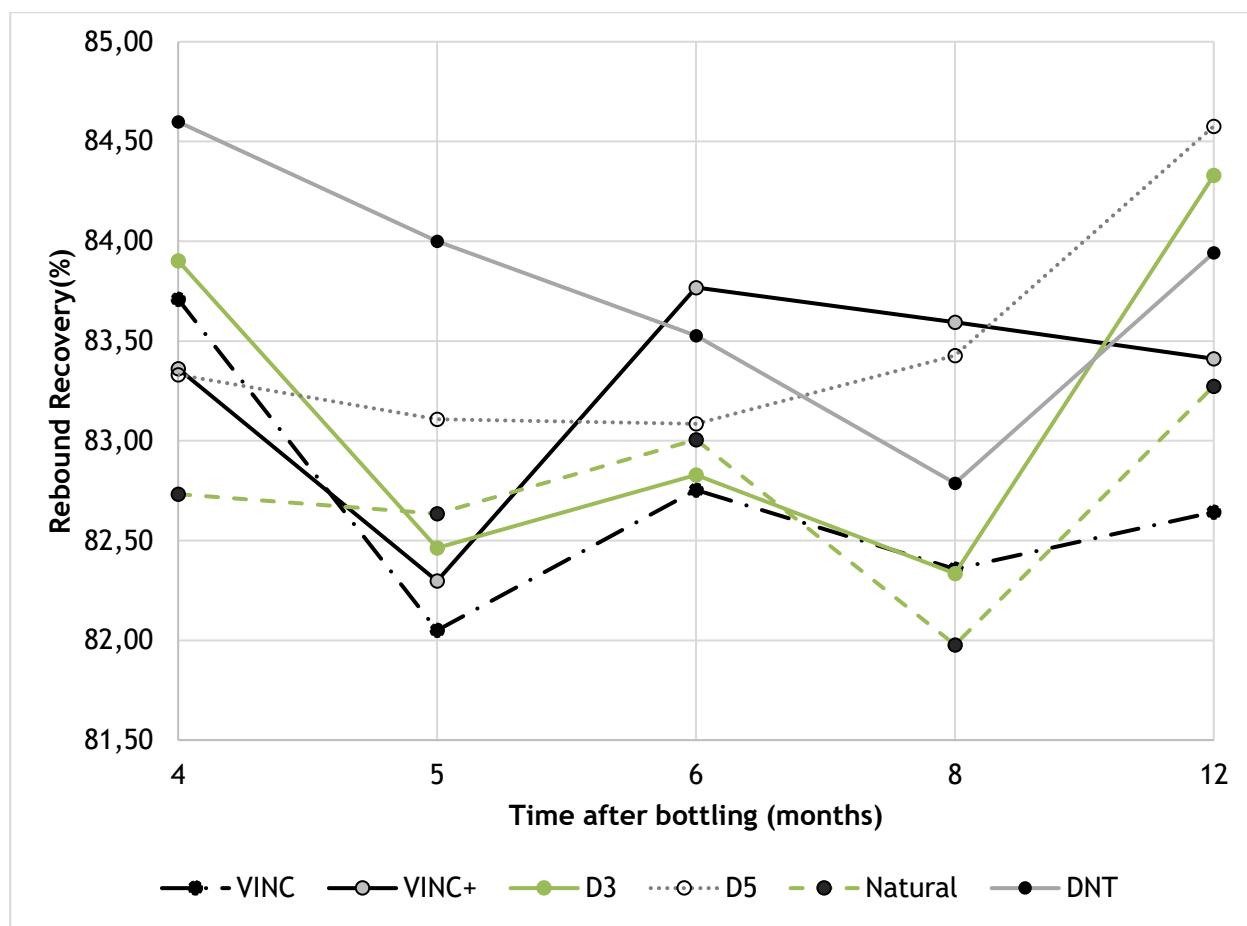


Figure A - 2 - Rebound Recovery during one year of bottling regarding all closures

Table A - 2 - Results of U Mann-Whitney for rebound recovery at 12 months

	VINC VINC+	VINC D3	VINC D5	VINC NAT	VINC DNT	VINC+ D3	VINC+ D5	VINC+ NAT	VINC+ DNT	D3 D5	D3 NAT	D3 DNT	D5 NAT	D5 DNT	NAT DNT
U Mann-Whitney	55.0	42.0	42.0	58.5	40.0	51.0	58.0	71.0	61.0	69.0	49.5	59.5	54.5	66.0	57.5
Z	-1.0	-1.7	-1.7	-0.8	-1.8	-1.2	-0.8	-0.1	-0.6	-1.2	-1.3	-0.7	-1.0	-0.3	-0.8
Sig.	0.33	0.08	0.08	0.44	0.07	0.23	0.42	0.95	0.53	0.86	0.19	0.47	0.31	0.73	0.40

* Orange shading are the values with sig> 0.05

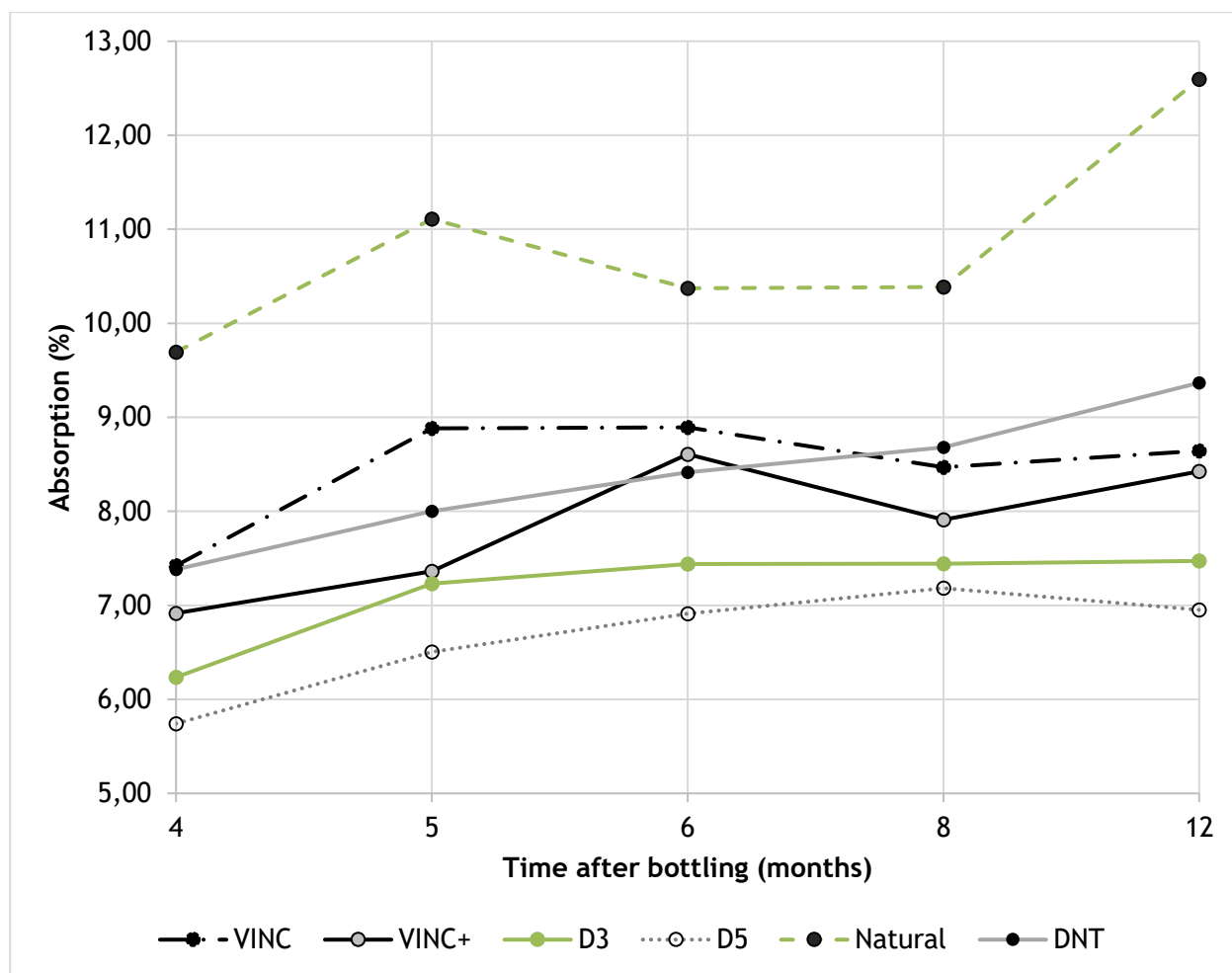


Figure A - 3 - Absorption during one year of bottling regarding all closures

Table A - 3 - Results of U Mann-Whitney for absorption after 12 months of bottling

	VINC VINC+	VINC D3	VINC D5	VINC NAT	VINC DNT	VINC+ D3	VINC+ D5	VINC+ NAT	VINC+ DNT	D3 D5	D3 NAT	D3 DNT	D5 NAT	D5 DNT	NAT DNT
U Mann-Whitney	62.0	1.5	0.0	7.0	24.0	12.0	4.0	5.0	14.5	26.0	0.0	0.0	0.0	0.0	23.0
Z	-0.6	-4.1	-4.2	-3.8	-2.7	-3.5	-3.9	-3.9	-3.3	-2.7	-4.2	-4.2	-4.2	-4.2	-2.8
Sig.	0.56	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01

* Orange shading are the values with sig> 0.05

Annex B - Data of Sensorial Analysis

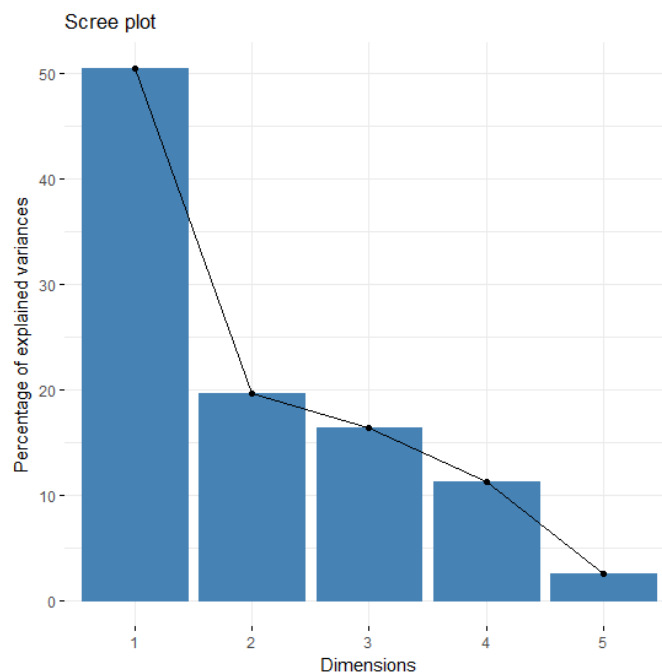


Figure B - 1 - Scree Plot of MFA from White Wine at 8 months

Table B - 1 - MFA data of white wine after 8 months of bottling

	Dim. 1	ctr (%)	Dim.2	ctr (%)
VINC	-0.574	0.497	1.299	6.548
VINC+	-4.210	26.772	-1.670	10.829
D3	-3.503	18.526	-1.313	6.688
D5	-0.159	0.038	4.029	63.014
NATURAL	4.541	31.138	-1.711	11.359
DNT	3.905	23.028	-0.634	1.562

*ctr - contribution of the sample on the construction of the dimension (axe)

**Dim. 1 dimension 1; Dim. 2 - dimension 2

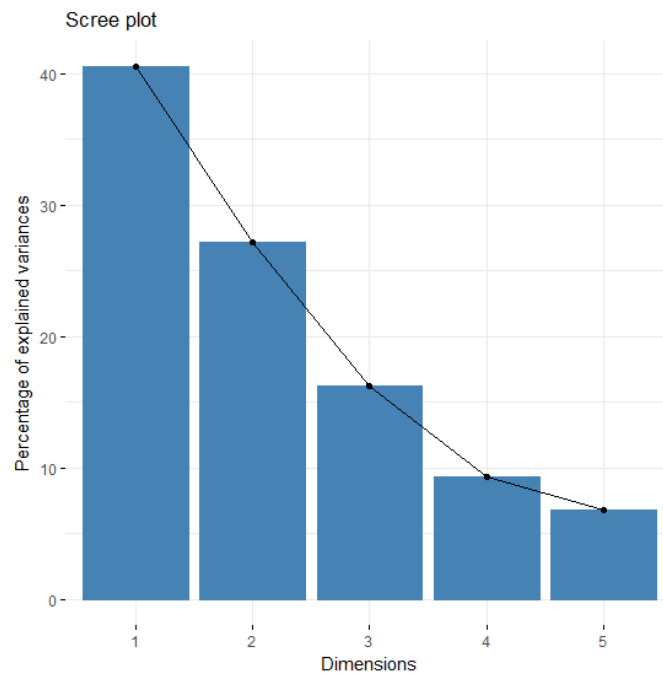


Figure B - 2 - Scree Plot of MFA from Red Wine at 8 months

Table B - 2 - MFA data of red wine after 8 months of bottling

	Dim. 1	ctr (%)	Dim.2	ctr (%)
VINC	-1.662	5.462	-4.173	51.332
VINC+	4.088	33.033	0.919	2.488
D3	2.863	16.200	1.487	6.517
D5	1.209	2.887	-2.189	14.117
NATURAL	-2.828	15.810	2.627	20.339
DNT	-3.669	26.607	1.329	5.206

*ctr - contribution of the sample on the construction of the dimension (axe)

**Dim. 1 - dimension 1; Dim. 2 - dimension 2

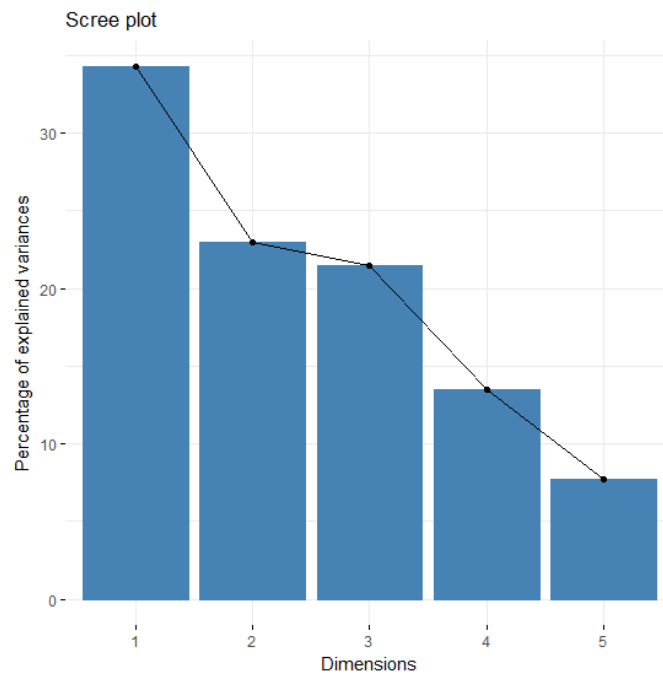


Figure B - 3 - Scree Plot of MFA from White Wine at 12 months

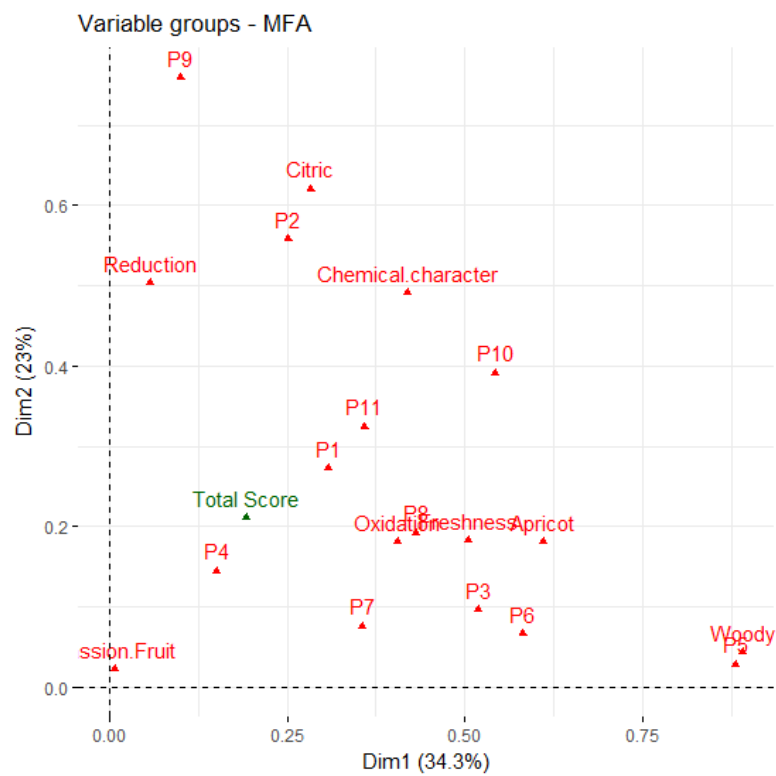


Figure B - 4 - Variable groups - White Wine 12 months

Table B - 3 - MFA data of white wine after 12 months of bottling

	Dim. 1	ctr (%)	Dim.2	ctr (%)
VINC	-0.088	0.017	-4.154	56.020
VINC+	1.796	7.018	2.559	21.264
D3	3.187	22.109	0.169	0.093
D5	-0.570	0.707	2.249	16.420
NATURAL	-5.544	66.913	0.475	0.732
DNT	1.219	3.236	-1.298	5.471

*ctr - contribution of the sample on the construction of the dimension (axe)

**Dim. 1 - dimension 1; Dim. 2 - dimension 2

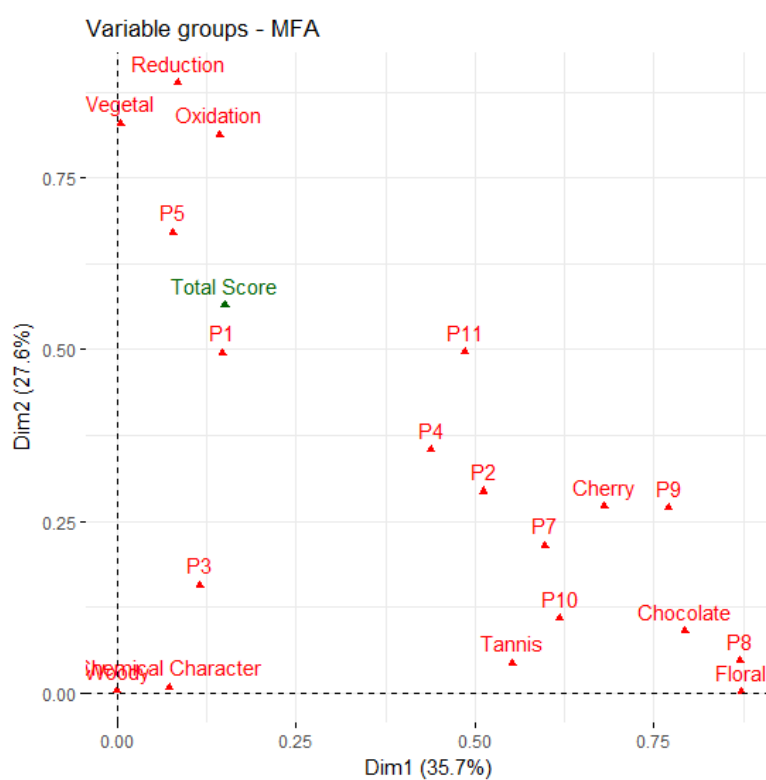


Figure B - 5 - Variables groups - Red Wine 12 months

Table B - 4 - MFA data of red wine after 12 months of bottling

	Dim. 1	ctr (%)	Dim.2	ctr (%)
VINC	2.373	11.970	-4.958	67.706
VINC+	-1.695	6.112	-0.504	0.701
D3	-2.022	8.692	0.733	1.478
D5	-2.011	8.596	1.250	4.300
NATURAL	5.197	57.421	3.028	25.252
DNT	-1.841	7.209	0.453	0.564

*ctr - contribution of the sample on the construction of the dimension (axe)

** Dim. 1 - dimension 1; Dim. 2 - dimension 2

6.1 R CODE (EXAMPLE) - MFA ANALYSIS

```
> Red8 <-
+   readXL("C:/Users/Maria/Google Drive/Tese de mestrado_ CorkSupply/Desenvolvimento da
Tese/ESTATÍSTICA/TRATAMENTO DE RESULTADOS NAPPING/21 Nov Resultados_Totais.xls",
+   rownames=FALSE, header=TRUE, na="", sheet="TINTO", stringsAsFactors=TRUE)
> editDataset(Red8)
> library(FactoMineR)
> data(Red8)
> res <- MFA(Red8, group=c(rep(2,9), rep(1,10)), type=c(rep("s",19)), name.group=c("P1", "P2",
"P3", "P4", "P5", "P6", "P7", "P8", "P9", "Vegetal", "Fruty", "Reduction", "Chemical character",
"Tannis", "Cherry", "Floral", "Chocolate", "Woody", "Total Score"), num.group.sup=c(19),
graph=FALSE)
> summary(res)
> library("factoextra")
> fviz_screplot(res)
> fviz_mfa_var(res, "group")
> plot(res, choix = "ind", habillage="ind")>
> plot(res, choix = "ind", habillage="ind")
> BB <-
```

```

+ readXL("C:/Users/Maria/Google Drive/Tese de mestrado_ CorkSupply/Desenvolvimento da
Tese/ESTATÍSTICA/TRATAMENTO DE RESULTADOS NAPPING/21 Nov Resultados_Totais.xls",
+ rownames=FALSE, header=TRUE, na="", sheet="Folha2", stringsAsFactors=TRUE)
> editDataset(BB)
> hc = hclust(dist(BB))
> plot(hc)
> library(factoextra)
> res.pca <- prcomp(BB, scale = TRUE)
> fviz_pca_ind(res.pca, col.ind = "cos2", gradient.cols = c("#00AFBB", "#E7B800", "#FC4E07"), repel
= TRUE)
> fviz_pca_var(res.pca, col.var = "contrib", gradient.cols = c("#00AFBB", "#E7B800", "#FC4E07"),
repel = TRUE)
> fviz_pca_biplot(res.pca, repel = TRUE, col.var = "#2E9FDF", col.ind = "#00AFBB"

```